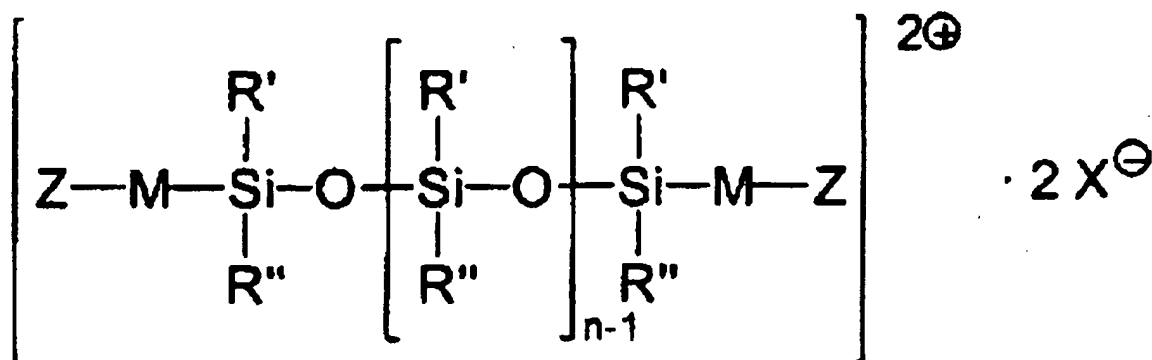


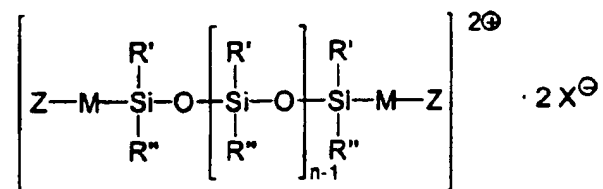
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(54) COMPOSITIONS D'AIDE AU RINCAGE
(54) RINSE AID COMPOSITIONS



(57) The use of diquatary polysiloxanes in detergents for machine dishwashing brings about advantageous effects, especially when the diquatary polysiloxanes are employed in the rinse cycle. Preferred diquatary polysiloxanes may be described by the formula I: (see formula I) in which Z is a quaternized nitrogen center, R' and R'' independently of one another are a C₁₋₄ alkyl radical or an aryl radical, M is a divalent hydrocarbon radical with at least 4 carbon atoms, which preferably has at least one hydroxyl group and may be interrupted by one or more oxygen atoms and/or groups of the type -C(O)-, -C(O)O- or -C(O)N-, n is a number from 1 to 201, and X⁻ is an organic or inorganic anion.

Abstract

The use of diquatertiary polysiloxanes in detergents for machine dishwashing brings about advantageous effects, especially when the diquatertiary polysiloxanes are employed in the rinse cycle. Preferred diquatertiary polysiloxanes may be described by the formula I:



in which Z is a quaternized nitrogen center, R' and R'' independently of one another are a C₁₋₄ alkyl radical or an aryl radical, M is a divalent hydrocarbon radical with at least 4 carbon atoms, which preferably has at least one hydroxyl group and may be interrupted by one or more oxygen atoms and/or groups of the type -C(O)-, -C(O)O- or -C(O)N-, n is a number from 1 to 201, and X⁻ is an organic or inorganic anion.

RINSE AID COMPOSITIONS

Field of the Invention

5 The present invention relates to the use of diquaternary polysiloxanes in detergent and rinse aid compositions for machine dishwashing. The present invention further relates to rinse aid compositions for machine dishwashing and to commercial forms which provide detergent and rinse aid in one product, and also to the processes for
10 preparing such rinse aid and detergent compositions.

Background of the Invention

Frequently, more stringent requirements are nowadays imposed on machine-washed kitchen- and tableware than on
15 handwashed ware. For instance, even ware which has been completely cleaned of food residues is not considered flawless when, following machine dishwashing, it still has whitish spots deriving from water hardness or other mineral salts and originating from dried water droplets
20 for lack of wetting agent.

In order to obtain sparkling and spotless ware, rinse aids are nowadays used successfully. The addition of
25 rinse aid at the end of the wash program ensures that the water runs off from the ware as completely as possible, so that at the end of the wash program the different surfaces are free from residues and gleam immaculately.

The machine cleaning of kitchen- and tableware in
30 domestic dishwashing machines normally involves a prewash cycle, a main wash cycle and a rinse cycle, interspersed with intermediate wash cycles. With the majority of machines, the prewash cycle may be selected for highly soiled ware, but is selected by the user only in
35 exceptional cases, so that in the majority of machines a main wash cycle, an intermediate wash cycle with clean water, and a rinse cycle are conducted. The temperature

of the main wash cycle varies, according to machine type and program step choice, between 40 and 65°C. In the rinse cycle, rinse aid compositions are added from a dosing tank within the machine, these rinse aids normally comprising nonionic surfactants as their principal constituent. Rinse aids of this kind are in liquid form and have been widely described in the prior art. Their primary object is to prevent lime spots and deposits on the cleaned ware. Besides water and low-foaming nonionic surfactants, these rinse aids often also include hydrotropes, pH modifiers such as citric acid, or scale-inhibiting polymers.

EP-B1 0 197 434 (Henkel) discloses liquid rinse aids comprising mixed ethers as nonionic surfactants. A large number of different materials (glass, metal, silver, plastic, porcelain) are cleaned in the dishwashing machine. This diversity of materials must be wetted as thoroughly as possible in the rinse cycle. Rinse aid formulations comprising exclusively mixed ethers as the surfactant component fail completely or adequately to meet these requirements, so that the rinse-clean effect or drying effect, especially in the case of plastics surfaces, is unsatisfactory.

The reservoir tank within the dishwashing machine has to be filled up at regular intervals with rinse aid, one fill being sufficient for from 10 to 50 cycles, depending on machine type. If the user forgets to fill up the tank, then glasses, in particular, acquire unsightly lime spots and deposits. In the prior art, therefore, there exist a number of proposals for integrating a rinse aid into the machine dishwashing detergent. These proposals are tied to the commercial form of the compact tablet.

For instance, European Patent Application **EP-A-0 851 024** (Unilever) describes two-layer detergent tablets whose

first layer comprises peroxy bleach, builder and enzyme while the second layer comprises acidifiers, a continuous medium having a melting point of between 55 and 70°C, and scale inhibitors. It is intended that the high-melting continuous medium will effect retarded release of the acid(s) and scale inhibitor(s) to produce a rinse aid effect. This document makes no mention of powder-form machine dishwashing compositions or rinse aid systems comprising surfactant.

The prior German Patent Application DE 198 51 426.3 (Henkel KGaA) describes a process for producing multiphase detergent tablets which comprises compressing a particulate premix into tablets which have a depression, which is subsequently filled with a separately prepared melt suspension or melt emulsion comprising a coating substance and one or more active substances suspended or dispersed therein.

Summary of the Invention

One commercial form which may be used both separately as a rinse aid in solid form to be dosed by the user, and as an admix component to pulverulent machine dishwashing compositions is described in the prior German Patent Application DE 199 14 364.1 (Henkel KGaA).

It is an object of the present invention to provide new rinse aids which in terms of their performance properties provide results at least equal to those of customary commercial rinse aids and which, furthermore, bring additional performance advantages. The new rinse aids ought to be suitable for use both as conventional rinse aid compositions and in the form of combination products and ought to develop their advantageous properties irrespective of the type of formulation. Not least, the new rinse aid compositions should also be suitable for use in conventional machine dishwashing detergents, i.e.,

in the form of an additive component, too, the compositions ought to permit performance advantages.

It has now been found that the use of diquatarnary polysiloxanes in machine dishwashing detergents brings
5 about advantageous effects. It is particularly advantageous if the diquatarnary polysiloxanes are employed in the rinse cycle.

10 In a first embodiment, therefore, the present invention provides for the use of diquatarnary polysiloxanes in machine dishwashing compositions.

The sole addition of these compounds to detergents results in ware items treated with such compositions
15 becoming much cleaner in subsequent washes than ware items washed with conventional compositions. This effect is independent of whether the machine dishwashing compositions are in liquid, powder, or tablet form.

20 An additional positive effect occurring is a shortening of the drying time of the ware items treated with the detergent, i.e., after the wash program has run, the user is able to take the ware from the machine, and use it again, sooner.

25 The invention is notable for an enhanced "cleanability" of the treated substrates on subsequent washes and for a considerable reduction in the drying time relative to comparable compositions without the use of diquatarnary polysiloxane. In addition to this primary effect of the
30 invention, the diquatarnary polysiloxane, as expected, displays the foam-suppressing activity inherent in the silicones. Surprisingly, moreover, liquid compositions which comprise diquatarnary polysiloxanes display a
35 cleaning power which is not only not adversely affected by the diquatarnary polysiloxane but indeed is usually

increased, and also an increased low-temperature stability in all cases.

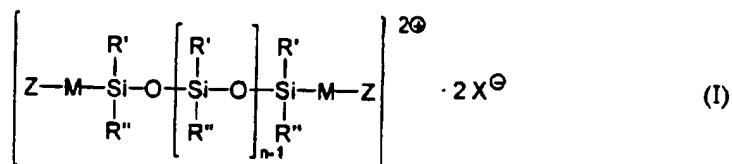
5 In the context of the teaching of the invention, drying time generally has its literal meaning; that is, it is the time which elapses until a ware surface treated in a dishwashing machine has dried, but in particular is the time which elapses until 90% of a surface treated with a detergent or rinse aid composition in concentrated or
10 dilute form has dried.

Diquaternary polysiloxanes for the purposes of the invention are polyorganosiloxanes (i.e., silicones) having two quaternized organic ammonium groups, i.e., two
15 quaternary nitrogen atoms, which each carry four organic radicals and are attached by each of these four radicals to one silicon atom of the polyorganosiloxane. In accordance with the invention, diquaternary polysiloxanes are used individually or as mixtures of different
20 diquaternary polysiloxanes in the composition or process.

It is particularly advantageous if the diquaternary polysiloxanes are present in the last cycle, i.e., in the rinse cycle. In this way, the advantageous action is not
25 weakened by subsequent cycles. The invention therefore additionally provides for the use of diquaternary polysiloxanes in the rinse cycle during machine dishwashing.

30 **Detailed Description of the Invention**

The diquaternary polysiloxanes used in accordance with the invention preferably comprise compounds of the formula I,



in which Z is a quaternized nitrogen center,

R' and R'' independently of one another are a C₁₋₄ alkyl radical or an aryl radical,

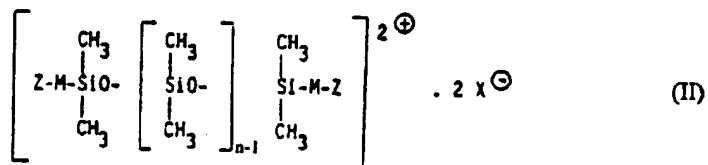
M is a divalent hydrocarbon radical with at least 4 carbon atoms, which preferably has at least one hydroxyl group and may be interrupted by one or more oxygen atoms and/or groups of the type -C(O)-, -C(O)O- or -C(O)N-,

n is a number from 1 to 201, and

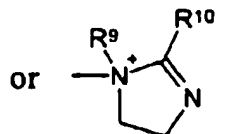
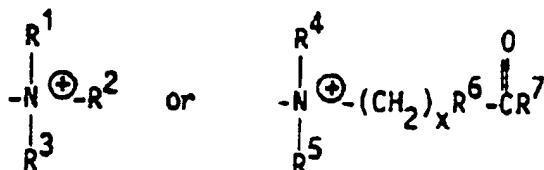
X⁻ is an organic or inorganic anion,

as are described, for example, in DE 37 19 086 C1 and EP 0 294 642 B1.

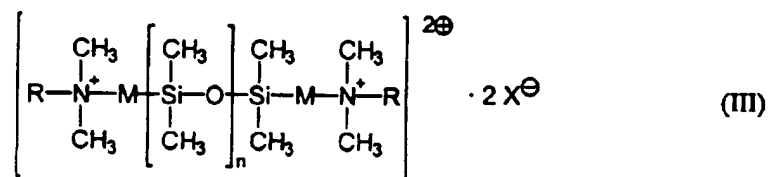
Particularly preferred diquaternary polysiloxanes used are the diquaternary poly(dimethylsiloxanes) of the formula II,



in which Z is the radical,



- $R^1, R^2, R^3, R^4, R^5, R^7, R^9$ and R^{10} independently of one another are C_{1-22} alkyl or C_{2-22} alkylene radicals without or with one or more hydroxyl groups or radicals $-CH_2$ -aryl, preferably at least one of the radicals R^1, R^2 and R^3 having at least 10 carbon atoms or one of the radicals R^1, R^2 and R^3 being a benzyl radical,
- R^6 is an oxygen atom or a group $-N(R^8)$, R^8 being a C_{1-4} alkyl or hydroxyalkyl radical or hydrogen,
- M is a divalent hydrocarbon radical with at least 4 carbon atoms, which preferably has at least one hydroxyl group and may be interrupted by one or more oxygen atoms and/or groups of the type $-C(O)-$, $-C(O)O-$ or $-C(O)N-$,
- n is a number from 1 to 201 and
- X^- is an organic or inorganic anion.
- These are, in particular, diquateryary poly(dimethylsiloxanes) of the formula III,



- in which R is a C_{6-22} alkyl or alkylene radical, especially a stearyl radical,
- M is a spacer of the formula $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_3$, the connectivity $\text{N}^+-\text{M}-\text{Si}$ of the spacer corresponding to $\text{N}^+-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_3-\text{Si}$,
- n is a number from 1 to 100, especially 10, 30 or 50, and
- X^- is an organic or inorganic anion, preferably an acetate ion.

5 Examples of anions that are suitable in accordance with the invention, in addition to acetate ions, include chloride ions, bromide ions, hydrogen sulfate ions, and sulfate ions.

10 The diquaternalary poly(dimethylsiloxanes) of the formula III which are particularly preferred in accordance with the invention, with stearyl radicals R, acetate ions X⁻ and values for n of 10, 30 and 50, respectively, are available as Tegopren® 6920, Tegopren® 6922 and Tegopren® 6924 from Th. Goldschmidt AG.

15 Further examples of diquaternalary polysiloxanes of the formula I to III that are suitable in accordance with the invention may be found in DE 37 19 086 C1 and EP 0 294 642 B1.

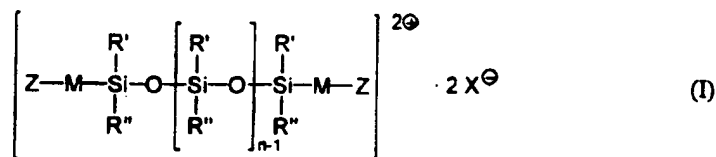
20 The use in accordance with the invention may be simply actualized by incorporating the aforementioned substances into liquid, powder or tablet detergents or into rinse aid compositions. Machine dishwashing compositions comprising diquaternalized polysiloxanes are likewise provided by the present invention.

25 In preferred embodiments of the present invention, the diquaternalized polysiloxanes are employed in the rinse cycle of machine dishwashing. Preferred further embodiments of the present invention therefore relate to
30 rinse aid compositions for machine dishwashing and to combination forms which combine detergent and rinse aid compositions with one another, the latter being offered in particular in powder or tablet form.

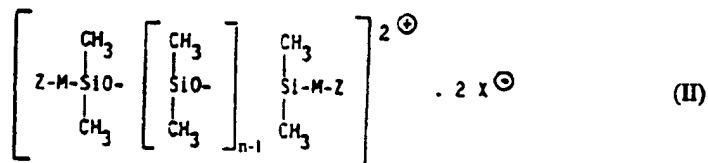
35 The present invention therefore additionally and preferably provides rinse aid compositions for machine dishwashing which comprise diquaternalary polysiloxanes.

As described above, such rinse aid compositions are placed by the user into the reservoir tank of the dishwashing machine, from where it is dosed automatically into the rinse cycle. Depending on the dosing volume and capacity of the tank, one tank fill is normally sufficient for from 10 to 50 rinse cycles.

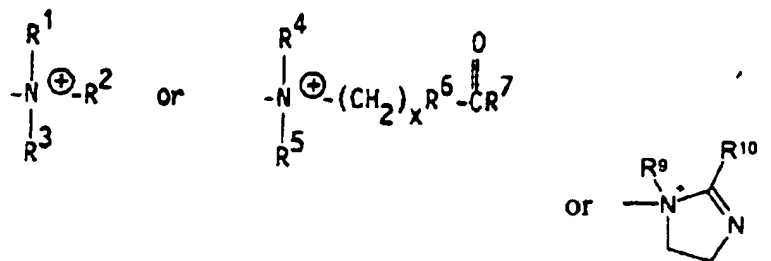
In analogy to the preferred use (see above), preference is also given to rinse aid compositions of the invention comprising one or more diquatertiary polysiloxanes of the formula I,



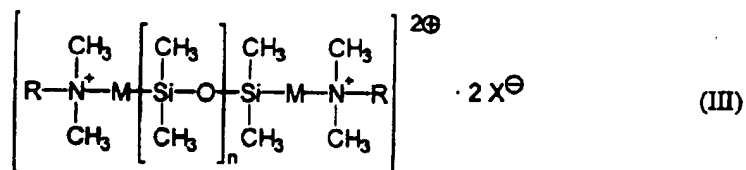
in which Z is a quaternized nitrogen center,
 R' and R'' independently of one another are a C₁₋₄ alkyl radical or an aryl radical,
 M is a divalent hydrocarbon radical with at least 4 carbon atoms, which preferably has at least one hydroxyl group and may be interrupted by one or more oxygen atoms and/or groups of the type -C(O)-, -C(O)O- or -C(O)N-,
 n is a number from 1 to 201, and
 X⁻ is an organic or inorganic anion,
 preference being given to rinse aid compositions comprising one or more diquatertiary poly(dimethylsiloxanes) of the formula II,



in which Z is the radical,



- 5 $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^7, \text{R}^9$ and R^{10} independently of one another are C_{1-22} alkyl or C_{2-22} alkylene radicals without or with one or more hydroxyl groups or radicals $-\text{CH}_2\text{-aryl}$, preferably at least one of the radicals R^1, R^2 and R^3 having at least 10 carbon atoms or one of the
- 10 radicals R^1, R^2 and R^3 being a benzyl radical,
- R^6 is an oxygen atom or a group $-\text{N}(\text{R}^8)$, R^8 being a C_{1-4} alkyl or hydroxyalkyl radical or hydrogen,
- M is a divalent hydrocarbon radical with at least 4 carbon atoms, which preferably has at least one
- 15 hydroxyl group and may be interrupted by one or more oxygen atoms and/or groups of the type $-\text{C}(\text{O})-$, $-\text{C}(\text{O})\text{O}-$ or $-\text{C}(\text{O})\text{N}-$,
- n is a number from 1 to 201 and
- X^- is an organic or inorganic anion,
- 20 and particular preference being given to those compositions comprising one or more diquatary poly(dimethylsiloxanes) of the formula III,



25

in which R is a C_{6-22} alkyl or alkylene radical, especially a stearyl radical,

M is a spacer of the formula $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_3$,

n is a number from 1 to 100, especially 10, 30 or 50, and
X⁻ is an organic or inorganic anion, preferably an acetate ion.

5

The amount of one or more diquatertiary polysiloxanes in the compositions of the invention may vary depending on the intended application and the desired product performance, with preferred rinse aid compositions of the invention comprising the diquatertiary polysiloxane(s) in amounts of from 0.001 to 20% by weight, preferably from 0.01 to 10% by weight, with particular preference from 0.1 to 5% by weight, and in particular from 0.15 to 2.5% by weight, based in each case on the rinse aid composition.

15

The compositions of the invention may, furthermore, as their surfactant component comprise anionic, nonionic, cationic and/or amphoteric surfactants, nonionic surfactants being preferred on account of their foaming capacity.

20

Anionic surfactants used are, for example, those of the sulfonate and sulfate type. Preferred surfactants of the sulfonate type are C₉₋₁₃ alkylbenzenesulfonates, olefinsulfonates, i.e., mixtures of alkenesulfonates and hydroxyalkanesulfonates, and also disulfonates, as are obtained, for example, from C₁₂₋₁₈ monoolefins having a terminal or internal double bond by sulfonating with gaseous sulfur trioxide followed by alkaline or acidic hydrolysis of the sulfonation products. Also suitable are alkanesulfonates, which are obtained from C₁₂₋₁₈ alkanes, for example, by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization, respectively. Likewise suitable, in addition, are the esters of α -sulfo fatty acids (ester sulfonates), e.g., the α -sulfonated

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methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids.

Further suitable anionic surfactants are sulfated fatty acid glycerol esters. Fatty acid glycerol esters are the monoesters, diesters and triesters, and mixtures thereof, as obtained in the preparation by esterification of a monoglycerol with from 1 to 3 mol of fatty acid or in the transesterification of triglycerides with from 0.3 to 2 mol of glycerol. Preferred sulfated fatty acid glycerol esters are the sulfation products of saturated fatty acids having 6 to 22 carbon atoms, examples being those of caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid, or behenic acid.

Preferred alk(en)yl sulfates are the alkali metal salts, and especially the sodium salts, of the sulfuric monoesters of C_{12} - C_{18} fatty alcohols, examples being those of coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or of C_{10} - C_{20} oxo alcohols, and those monoesters of secondary alcohols of these chain lengths. Preference is also given to alk(en)yl sulfates of said chain length which contain a synthetic straight-chain alkyl radical prepared on a petrochemical basis, these sulfates possessing degradation properties similar to those of the corresponding compounds based on fatty-chemical raw materials. From a detergents standpoint, the C_{12} - C_{16} alkyl sulfates and C_{12} - C_{15} alkyl sulfates, and also C_{14} - C_{15} alkyl sulfates, are preferred. In addition, 2,3-alkyl sulfates, which may be obtained as commercial products from the Shell Oil Company under the name DAN®, are suitable anionic surfactants.

Also suitable are the sulfuric monoesters of the straight-chain or branched C_{7-21} alcohols ethoxylated with

from 1 to 6 mol of ethylene oxide, such as 2-methyl-
branched C₉₋₁₁ alcohols containing on average 3.5 mol of
ethylene oxide (EO) or C₁₂₋₁₈ fatty alcohols containing
from 1 to 4 EO. Because of their high foaming behavior
5 they are used in detergents only in relatively small
amounts, for example, in amounts of from 1 to 5% by
weight.

Further suitable anionic surfactants include the salts of
10 alkylsulfosuccinic acid, which are also referred to as
sulfosuccinates or as sulfosuccinic esters and which
constitute monoesters and/or diesters of sulfosuccinic
acid with alcohols, preferably fatty alcohols and
especially ethoxylated fatty alcohols. Preferred
15 sulfosuccinates comprise C₈₋₁₈ fatty alcohol radicals or
mixtures thereof. Especially preferred sulfosuccinates
contain a fatty alcohol radical derived from ethoxylated
fatty alcohols which themselves represent nonionic
surfactants (for description, see below). Particular
20 preference is given in turn to sulfosuccinates whose
fatty alcohol radicals are derived from ethoxylated fatty
alcohols having a narrowed homolog distribution.
Similarly, it is also possible to use alk(en)ylsuccinic
acid having preferably 8 to 18 carbon atoms in the
25 alk(en)yl chain, or salts thereof.

Further suitable anionic surfactants are, in particular,
soaps. Suitable soaps include saturated fatty acid soaps,
such as the salts of lauric acid, myristic acid, palmitic
30 acid, stearic acid, hydrogenated erucic acid and behenic
acid, and, in particular, mixtures of soaps derived from
natural fatty acids, e.g., coconut, palm kernel or tallow
fatty acids.

35 The anionic surfactants, including the soaps, may be
present in the form of their sodium, potassium or
ammonium salts and also as soluble salts of organic

bases, such as mono-, di- or triethanolamine. Preferably, the anionic surfactants are in the form of their sodium or potassium salts, in particular in the form of the sodium salts.

5

Nonionic surfactants used are preferably alkoxyated, advantageously ethoxylated, especially primary, alcohols having preferably 8 to 18 carbon atoms and on average from 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in position 2 and/or may comprise linear and methyl-branched radicals in a mixture, as are commonly present in oxo alcohol radicals. In particular, however, preference is given to alcohol ethoxylates containing linear radicals from alcohols of natural origin having 12 to 18 carbon atoms, e.g., from coconut, palm, tallow fatty or oleyl alcohol and on average from 2 to 8 EO per mole of alcohol. Preferred ethoxylated alcohols include, for example, C₁₂₋₁₄ alcohols containing 3 EO or 4 EO, C₉₋₁₁ alcohol containing 7 EO, C₁₃₋₁₅ alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C₁₂₋₁₈ alcohols containing 3 EO, 5 EO or 7 EO, and mixtures thereof, such as mixtures of C₁₂₋₁₄ alcohol containing 3 EO and C₁₂₋₁₈ alcohol containing 5 EO. The stated degrees of ethoxylation represent statistical mean values, which for a specific product may be an integer or a fraction. Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NREs). In addition to these nonionic surfactants it is also possible to use fatty alcohols containing more than 12 EO. Examples thereof are tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO.

As further nonionic surfactants, furthermore, use may also be made of alkyl glycosides of the general formula RO(G)_x, where R is a primary straight-chain or methyl-branched aliphatic radical, especially an aliphatic

radical methyl-branched in position 2, containing 8 to 22, preferably 12 to 18, carbon atoms, and G is the symbol representing a glucose unit having 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization, x, which indicates the distribution of monoglycosides and oligoglycosides, is any desired number between 1 and 10; preferably, x is from 1.2 to 1.4.

A further class of nonionic surfactants used with preference, which are used either as sole nonionic surfactant or in combination with other nonionic surfactants, are alkoxyated, preferably ethoxyated, or ethoxyated and propoxyated, fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain. Nonionic surfactants of the amine oxide type, examples being N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamide type, may also be suitable. The amount of these nonionic surfactants is preferably not more than that of the ethoxyated fatty alcohols, in particular not more than half thereof.

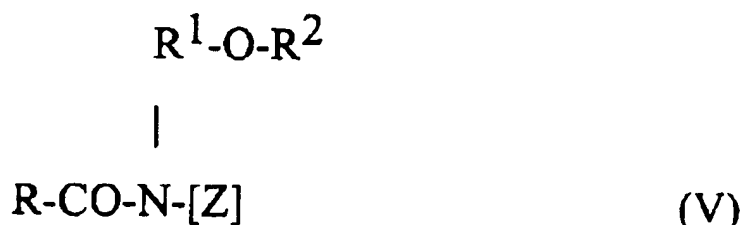
Further suitable surfactants are polyhydroxy fatty acid amides of the formula (IV)



where RCO is an aliphatic acyl radical having 6 to 22 carbon atoms, R^1 is hydrogen or an alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms, and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and from 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances which are customarily obtainable by reductive amination of a

reducing sugar with ammonia, an alkylamine or an alkanolamine, and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

- 5 The group of the polyhydroxy fatty acid amides also includes compounds of the formula (V)



- 10 where R is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R^1 is a linear, branched or cyclic alkyl radical or an aryl radical having 2 to 8 carbon atoms and R^2 is a linear, branched or cyclic alkyl radical or an aryl radical or an oxyalkyl radical having
15 1 to 8 carbon atoms, preference being given to C_{1-4} alkyl radicals or phenyl radicals, and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or alkoxyated, preferably ethoxylated or propoxylated, derivatives of
20 said radical.

- [Z] is preferably obtained by reductive amination of a reduced sugar, e.g., glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-
25 substituted compounds may be converted to the desired polyhydroxy fatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst.

- Preferred surfactants used are low-foaming nonionic surfactants. With particular preference, the detergent components of the invention for machine dishwashing comprise nonionic surfactants, especially nonionic surfactants from the group of the alkoxyated alcohols.

Nonionic surfactants used are preferably alkoxyated, advantageously ethoxylated, especially primary, alcohols having preferably 8 to 18 carbon atoms and on average from 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in position 2 and/or may comprise linear and methyl-branched radicals in a mixture, as are commonly present in oxo alcohol radicals. In particular, however, preference is given to alcohol ethoxylates containing linear radicals from alcohols of natural origin having 12 to 18 carbon atoms, e.g., from coconut, palm, tallow fatty or oleyl alcohol and on average from 2 to 8 EO per mole of alcohol. Preferred ethoxylated alcohols include, for example, C₁₂₋₁₄ alcohols containing 3 EO or 4 EO, C₉₋₁₁ alcohol containing 7 EO, C₁₃₋₁₅ alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C₁₂₋₁₈ alcohols containing 3 EO, 5 EO or 7 EO, and mixtures thereof, such as mixtures of C₁₂₋₁₄ alcohol containing 3 EO and C₁₂₋₁₈ alcohol containing 5 EO. The stated degrees of ethoxylation represent statistical mean values, which for a specific product may be an integer or a fraction. Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NREs). In addition to these nonionic surfactants it is also possible to use fatty alcohols containing more than 12 EO. Examples thereof are tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO.

Especially preferred rinse aid compositions of the invention are those that comprise a nonionic surfactant having a melting point above room temperature. Accordingly, preferred rinse aid compositions comprise nonionic surfactant(s) having a melting point above 20°C, preferably above 25°C, with particular preference between 25 and 60°C, and in particular between 26.6 and 43.3°C.

Suitable nonionic surfactants having melting or softening points within the stated temperature range are, for example, low-foaming nonionic surfactants which may be solid or highly viscous at room temperature. If nonionic surfactants which are highly viscous at room temperature are used, then it is preferred that they have a viscosity above 20 Pas, preferably above 35 Pas, and in particular above 40 Pas. Also preferred are nonionic surfactants which possess a waxlike consistency at room temperature.

Preferred nonionic surfactants for use that are solid at room temperature originate from the groups of alkoxyated nonionic surfactants, especially the ethoxylated primary alcohols, and mixtures of these surfactants with surfactants of more complex construction such as polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) surfactants. Such (PO/EO/PO) nonionic surfactants are notable, furthermore, for good foam control.

In one preferred embodiment of the present invention, the nonionic surfactant having a melting point above room temperature is an ethoxylated nonionic surfactant originating from the reaction of a monohydroxy alkanol or alkylphenol having 6 to 20 carbon atoms with preferably at least 12 mol, with particular preference at least 15 mol, in particular at least 20 mol, of ethylene oxide per mole of alcohol or alkylphenol, respectively.

A particularly preferred nonionic surfactant for use that is solid at room temperature is obtained from a straight-chain fatty alcohol having 16 to 20 carbon atoms (C_{16-20} alcohol), preferably a C_{18} alcohol, and at least 12 mol, preferably at least 15 mol, and in particular at least 20 mol of ethylene oxide. Of these, the so-called "narrow range ethoxylates" (see above) are particularly preferred.

Accordingly, particularly preferred rinse aid compositions of the invention comprise ethoxylated nonionic surfactant(s) obtained from C₆₋₂₀ mono-
5 hydroxyalkanols or C₆₋₂₀ alkylphenols or C₁₆₋₂₀ fatty alcohols and more than 12 mol, preferably more than 15 mol, and in particular more than 20 mol, of ethylene oxide per mole of alcohol.

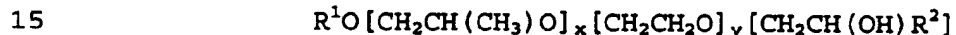
10 The nonionic surfactant which is solid at room temperature preferably further possesses propylene oxide units in the molecule. Preferably, such PO units account for up to 25% by weight, with particular preference up to 20% by weight, and in particular up to 15% by weight, of
15 the overall molecular mass of the nonionic surfactant. Particularly preferred nonionic surfactants are ethoxylated monohydroxy alkanols or alkylphenols, which additionally comprise polyoxyethylene-polyoxypropylene block copolymer units. The alcohol or alkylphenol moiety
20 of such nonionic surfactant molecules in this case makes up preferably more than 30% by weight, with particular preference more than 50% by weight, and in particular more than 70% by weight, of the overall molar mass of such nonionic surfactants. Preferred rinse aid
25 compositions comprise ethoxylated and propoxylated nonionic surfactants wherein the propylene oxide units in the molecule account for up to 25% by weight, preferably up to 20% by weight, and in particular up to 15% by weight, of the overall molecular mass of the nonionic
30 surfactant.

Further nonionic surfactants whose use is particularly preferred, with melting points above room temperature, contain from 40 to 70% of a polyoxypropylene/
35 polyoxyethylene/polyoxypropylene block polymer blend which comprises 75% by weight of an inverted block copolymer of polyoxyethylene and polyoxypropylene

containing 17 mol of ethylene oxide and 44 mol of propylene oxide and 25% by weight of a block copolymer of polyoxyethylene and polyoxypropylene, initiated with trimethylolpropane and containing 24 mol of ethylene oxide and 99 mol of propylene oxide per mole of trimethylolpropane.

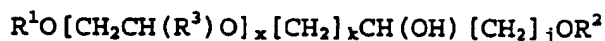
Nonionic surfactants which may be used with particular preference are, for example, obtainable under the name Poly Tergent® SLF-18 from Olin Chemicals.

A further preferred rinse aid composition of the invention comprises nonionic surfactants of the formula



in which R^1 is a linear or branched aliphatic hydrocarbon radical having 4 to 18 carbon atoms, or mixtures thereof, R^2 is a linear or branched hydrocarbon radical having 2 to 26 carbon atoms, or mixtures thereof, and x is between 0.5 and 1.5, and y is at least 15.

Further nonionic surfactants which may be used with preference are the endgroup-capped poly(oxyalkylated) nonionic surfactants of the formula

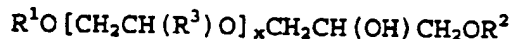


in which R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having 1 to 30 carbon atoms, R^3 is H or a methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl or 2-methyl-2-butyl radical, x is between 1 and 30, k and j are between 1 and 12, preferably between 1 and 5. Where $x \geq 2$, each R^3 in the above formula may be different. R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having 6 to 22

carbon atoms, radicals having 8 to 18 carbon atoms being particularly preferred. For the radical R^3 , H, $-CH_3$ or $-CH_2CH_3$ are particularly preferred. Particularly preferred values for x lie within the range from 1 to 20, in particular from 6 to 15.

As described above, each R^3 in the above formula may be different if $x \geq 2$. By this means it is possible to vary the alkylene oxide unit in the square brackets. If x, for example, is 3, the radical R^3 may be selected in order to form ethylene oxide ($R^3 = H$), or propylene oxide ($R^3 = CH_3$) units, which may be added on to one another in any sequence, examples being (EO)(PO)(EO), (EO)(EO)(PO), (EO)(EO)(EO), (PO)(EO)(PO), (PO)(PO)(EO) and (PO)(PO)(PO). The value of 3 for x has been chosen by way of example in this case and it is entirely possible for it to be larger, the scope for variation increasing as the values of x go up and embracing, for example, a large number of (EO) groups, combined with a small number of (PO) groups, or vice versa.

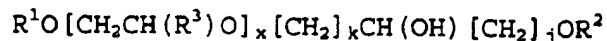
Particularly preferred endgroup-capped poly(oxyalkylated) alcohols of the above formula have values of $k = 1$ and $j = 1$, thereby simplifying the above formula to



In the last-mentioned formula, R^1 , R^2 and R^3 are as defined above and x stands for numbers from 1 to 30, preferably from 1 to 20, and in particular from 6 to 18. Particular preference is given to surfactants wherein the radicals R^1 and R^2 have 9 to 14 carbon atoms, R^3 is H, and x adopts values from 6 to 15.

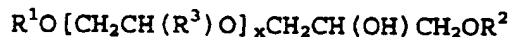
Summarizing the last-mentioned statements, preference is given to rinse aid compositions of the invention

comprising endgroup-capped poly(oxyalkylated) nonionic surfactants of the formula



5

in which R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having 1 to 30 carbon atoms, R^3 is H or a methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl or 2-methyl-2-butyl radical, x is between 1 and 30, k and j are between 1 and 12, preferably between 1 and 5, particular preference being given to surfactants of the type



15

where x is from 1 to 30, preferably from 1 to 20, and in particular from 6 to 18.

Instead of the aforementioned surfactants, or in conjunction with them, it is also possible to use cationic and/or amphoteric surfactants. In summary, preference is given to rinse aid compositions of the invention comprising surfactant(s), preferably nonionic surfactant(s), and especially nonionic surfactant(s) from the group of the alkoxyated alcohols, in amounts of from 0.1 to 40% by weight, preferably from 0.5 to 30% by weight, with particular preference from 1 to 20% by weight, and in particular from 2 to 15% by weight, based in each case on the rinse aid composition.

30

Nonaqueous solvents which may be used in the compositions of the invention come, for example, from the group of monohydric or polyhydric alcohols, alkanolamines or glycol ethers, provided they are miscible with water in the stated concentration range. The solvents are preferably selected from the ethanol, n- or i-propanol, butanols, glycol, propane- or butanediol, glycerol,

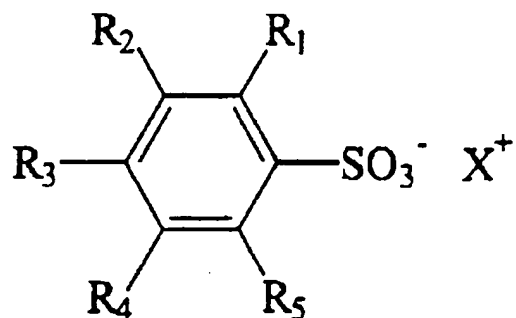
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diglycol, propyl- or butyldiglycol, hexylene glycol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, 5 diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ether, dipropylene glycol methyl or ethyl ether, methoxy-, ethoxy- or butoxytriglycol, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol t-butyl ether, and mixtures of these 10 solvents groups, so that preferred rinse aid compositions are those comprising nonaqueous solvent(s), preferably ethanol, n-propanol, i-propanol, 1-butanol, 2-butanol, glycol, propanediol, butanediol, glycerol, diglycol, propyl diglycol, butyl diglycol, hexylene glycol, 15 ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ether, dipropylene glycol methyl or ethyl 20 ether, methoxy-, ethoxy- or butoxytriglycol, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol t-butyl ether, and mixtures of these solvents.

25 The rinse aid compositions of the present invention may further comprise hydrotropes. The effect of adding such substances is that a substance of poor solubility becomes soluble in water in the presence of the hydrotrope, which is not itself a solvent. Substances which bring about 30 such an improvement in solubility are known as hydrotropes or hydrotropic agents. Typical hydrotropes, for example, in the formulation of liquid laundry detergents or cleaning products, are xylene-sulfonate and cumenesulfonate. Other substances, e.g., urea or 35 N-methylacetamide, raise the solubility through a structure-disrupting effect, where the water structure in

the environment of the hydrophobic group of a poorly soluble substance is broken down.

5 Rinse aid compositions that are preferred in the context of the present invention comprise solubilizers, preferably aromatic sulfonates of the formula



10 in which each of the radicals R_1 , R_2 , R_3 , R_4 and R_5 independently of one another is selected from H or a C_{1-5} alkyl or alkenyl radical and X is a cation.

15 Preferred substituents R_1 , R_2 , R_3 , R_4 and R_5 are selected independently of one another from H or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl or neo-pentyl radical. In general, at least three of said radicals R_1 to R_5 are hydrogen atoms, preference being given to aromatic sulfonates in
20 which three or four substituents on the aromatic ring are hydrogen atoms. The remaining radical or the remaining two radicals may adopt any position with respect to the sulfonate group and to one another. In the case of monosubstituted compounds of the formula I, it is
25 preferred if the radical R_3 is an alkyl radical while R_1 , R_2 , R_4 and R_5 are H (para-substitution).

30 Particularly preferred aromatic sulfonates in the context of the present invention are toluene-, cumene- or xylenesulfonate.

Of the two industrially available toluenesulfonates (ortho- and para-toluenesulfonate), the para isomer is preferred in the context of the present invention. With the cumenesulfonates, as well, the para-isopropylbenzenesulfonate is the preferred compound. Since xylene is used industrially usually as an isomer mixture, the industrially available xylenesulfonate is also a mixture of a plurality of compounds which result from the sulfonation of ortho-, meta- and para-xylene. Predominant in these isomer mixtures are the compounds in which, in each case, the following radicals in the above general formula are methyl groups (all other radicals are H): R_1 and R_2 , R_1 and R_4 , R_1 and R_3 , and R_1 and R_5 . In the case of the xylenesulfonates, accordingly, there is preferably at least one methyl group ortho to the sulfonate group.

X in the general formula indicated above is a cation, for example, an alkali metal cation such as sodium or potassium. X may alternatively be the charge-equivalent fraction of a polyvalent cation, for example, $Mg^{2+}/2$ or $Al^{3+}/3$, preference among the aforementioned cations being given to sodium.

In accordance with the invention, the sulfonates are used preferably in amounts of from 0.2 to 10% by weight, more preferably from 0.3 to 5% by weight, and in particular from 0.5 to 3% by weight, based in each case on the rinse aid composition.

Acidifiers as well may be added to the rinse aid compositions of the invention in order to lower the pH of the liquor in the rinse cycle. Appropriate compounds here include both organic and inorganic acids, provided they are compatible with the other ingredients. For reasons of protecting the consumer and of safe handling, the solid

mono-, oligo- and polycarboxylic acids may be used in particular. Preferred in turn from this group are citric acid, tartaric acid, succinic acid, malonic acid, adipic acid, maleic acid, fumaric acid, oxalic acid, and polyacrylic acid. Organic sulfonic acids such as amidosulfonic acid may likewise be used. A commercially available compound which is likewise preferred for use as an acidifier in the context of the present invention is Sokalan® DCS (trademark of BASF), a mixture of succinic acid (max. 31% by weight), glutaric acid (max. 50% by weight) and adipic acid (max. 33% by weight). Rinse aid compositions comprising acidifiers, preferably organic acids, with particular preference adipic acid, amidosulfonic acid, succinic acid, citric acid, fumaric acid, maleic acid, malonic acid, oxalic acid, and tartaric acid, and also mixtures of these acids, are preferred embodiments of the present invention.

In addition, the rinse aid compositions of the invention may preferably include one or more substances from the groups of the soil release polymers, the dyes, and the fragrances. These are described in detail later on below.

The rinse aid compositions described above are suitable for dosing via the reservoir tank of standard commercial dishwashing machines. The use of the diquaternalary polysiloxanes that is preferred in accordance with the invention may, however, also be actualized by providing dissolution-retarded forms which are metered into the dishwashing machine by the user before the beginning of the wash, but which do not release the active substances until the rinse cycle. This has the advantage that the user need only add one product, instead of two as previously.

The present invention further provides, in addition, a particulate rinse aid for machine dishwashing, comprising

- a) from 0 to 65% by weight of one or more support materials,
b) from 30 to 70% by weight of coating substance(s) having a melting point of more than 50°C,
5 c) from 0 to 65% by weight of fatty substance(s),
d) from 0 to 50% by weight of further active substances and/or auxiliaries, and
e) from 0.1 to 70% by weight of diquaternary polysiloxane.

10

Suitable support materials a) are all substances which are solid at room temperature. Normally, the substances selected will be those which develop an additional activity in the wash, builders being particularly
15 appropriate. In preferred particulate rinse aids containing support materials, the support materials present comprise substances from the group of the water-soluble detergent ingredients, preferably carbonates, hydrogen carbonates, sulfates, phosphates, and the
20 organic oligocarboxylic acids that are solid at room temperature, in amounts of from 35 to 60% by weight, preferably from 40 to 55% by weight, and in particular from 45 to 50% by weight, based in each case on the particle weight.

25

The abovementioned preferred support materials are described in detail later on below.

The particulate rinse aids may also be formulated without
30 support materials and thus consist only of ingredients b) to e). Such components are generally produced by shaping a melted mixture of the ingredients. Rinse aid particles containing support material may be obtained, for example, by spraying or pouring such a melt onto the support
35 materials.

The production processes are described later on below; there now follows a description of the ingredients b) to d), the amounts relating to rinse aid particles without support material. If support-material-based particles are to be produced, the data below refer to the composition of the mixture/melt that is applied to the supports, the fraction in the particle resulting from the fractions of mixture and of support material in the particle.

The coating substances used in the rinse aid compositions of the invention are subject to a variety of requirements, relating on the one hand to the melting behavior or, respectively, solidification behavior but on the other hand also to the material properties of the coating in the solidified state, i.e., in the rinse aid particles. Since the rinse aid particles are to be durably protected against ambient influences in transit or storage, the coating substance must possess a high stability with respect, for example, to impacts occurring in the course of packaging or transport. The coating substance should, therefore, have either at least partially elastic or at least plastic properties, in order to react by elastic or plastic deformation to any impact that does occur, and not to become crushed. The coating substance should have a melting range (solidification range) situated within a temperature range in which the active ingredients to be coated are not exposed to any excessive thermal load. On the other hand, however, the melting range must be sufficiently high still to offer effective protection for the enclosed active substances at least at slightly elevated temperature. In accordance with the invention, the coating substances have a melting point above 30°C.

It has proven advantageous for the coating substance not to exhibit a sharply defined melting point, as encountered commonly with pure, crystalline substances,

but instead to have a melting range which covers, in some cases, several degrees Celsius.

5 The coating substance preferably has a melting range which lies between about 45°C and about 75°C. In the present case that means that the melting range occurs within the stated temperature interval, and does not denote the width of the melting range. The width of the melting range is preferably at least 1°C, more preferably
10 from about 2 to about 3°C.

The abovementioned properties are in general possessed by what are called waxes. The term "waxes" is applied to a range of natural or synthetic substances which melt
15 without decomposition, generally at above 40°C, and are of comparatively low viscosity, without stringing, even at just a little above the melting point. They have a highly temperature-dependent consistency and solubility.

20 According to their origin, the waxes are divided into three groups: the natural waxes, chemically modified waxes, and the synthetic waxes.

The natural waxes include, for example, plant waxes such
25 as candelilla wax, carnauba wax, Japan wax, esparto grass wax, cork wax, guaruma wax, rice germ oil wax, sugar cane wax, ouricury wax, or montan wax, animal waxes such as beeswax, shellac wax, spermaceti, lanolin (wool wax), or uropygial grease, mineral waxes such as ceresin or
30 ozokerite (earth wax), or petrochemical waxes such as petrolatum, paraffin waxes or microcrystalline waxes.

The chemically modified waxes include, for example, hard
waxes such as montan ester waxes, sassol waxes, or
35 hydrogenated jojoba waxes.

By synthetic waxes are meant, in general, polyalkylene waxes or polyalkylene glycol waxes. As coating material it is also possible to use compounds from other classes of substance which meet the stated requirements in terms of softening point. Examples of synthetic compounds which have proven suitable are higher esters of phthalic acid, especially dicyclohexyl phthalate, which is available commercially under the name Unimoll® 66 (Bayer AG). Also suitable are synthetically prepared waxes from lower carboxylic acids and fatty alcohols, an example being dimyristyl tartrate, which is available under the name Cosmacol® ETLP (Condea). Conversely, synthetic or partially synthetic esters of lower alcohols with fatty acids from natural sources may also be used. This class of substance includes, for example, Tegin® 90 (Goldschmidt), a glyceryl monostearate palmitate. Shellac as well, for example, Schellack-KPS-Dreiring-SP (Kalkhoff GmbH), may be used according to the invention as a coating material.

Likewise counted among the waxes in the context of the present invention are, for example, the so-called wax alcohols. Wax alcohols are relatively high molecular mass, water-insoluble fatty alcohols having in general from about 22 to 40 carbon atoms. The wax alcohols occur, for example, in the form of wax esters of relatively high molecular mass fatty acids (wax acids) as a principal constituent of many natural waxes. Examples of wax alcohols are lignoceryl alcohol (1-tetracosanol), cetyl alcohol, myristyl alcohol, and melissyl alcohol. The coating of the particulate solids coated in accordance with the invention may, if desired, also include wool wax alcohols, by which are meant triterpenoid and steroid alcohols, an example being lanolin, which is available under the commercial designation Argowax® (Parentier & Co.), for example. Likewise possible for use, at least proportionally, as a constituent of the coating are, in

the context of the present invention, fatty acid glycerol esters or fatty acid alkanolamides, and also, if desired, water-insoluble or only sparingly water-soluble polyalkylene glycol compounds.

5

Preferably, the coating substance particles present in the rinse aid of the invention comprises a predominant paraffin wax fraction. That means that at least 50% by weight of the total coating substances present, preferably more, consist of paraffin wax. Particularly
10 suitable are paraffin wax contents (based on total coating substance) of approximately 60% by weight, approximately 70% by weight or approximately 80% by weight, with even higher proportions, of, for example,
15 more than 90% by weight being particularly preferred. In one particular embodiment of the invention, the total amount of the coating substance used consists exclusively of paraffin wax.

20 Relative to the other, natural waxes mentioned, paraffin waxes have the advantage in the context of the present invention that in an alkaline detergent environment there is no hydrolysis of the waxes (as is to be expected, for example, with the wax esters), since paraffin wax
25 contains no hydrolyzable groups.

Paraffin waxes consist primarily of alkanes, with small fractions of isoalkanes and cycloalkanes. The paraffin for use in accordance with the invention preferably
30 contains essentially no constituents having a melting point above 70°C, with particular preference above 60°C. Below this melting temperature, in the detergent liquor, fractions of high-melting alkanes in the paraffin may leave unwanted wax residues on the surfaces to be cleaned
35 or on the ware to be cleaned. Wax residues of this kind lead in general to an unattractive appearance of the cleaned surface and should therefore be avoided.

Preferred particulate rinse aids comprise as coating substance at least one paraffin wax having a melting range of from 50°C to 60°C.

5

Preferably, the amount of alkanes, isoalkanes and cycloalkanes which are solid at ambient temperature (generally from about 10 to about 30°C) in the paraffin wax used is as high as possible. The larger the amount of solid wax constituents in a wax at room temperature, the more useful that wax is in the context of the present invention. As the proportion of solid wax constituents increases, there is an increase in the resistance of the rinse aid particles to impacts or friction against other surfaces, resulting in a longer-lasting protection of the particles of active substances. High proportions of oils or liquid wax constituents may cause weakening of the particles as a result of which pores are opened and the active substances are exposed to the ambient influences mentioned at the outset.

In addition to paraffin, the coating substance may further comprise one or more of the abovementioned waxes or waxlike substances as main ingredient. In principle, the mixture forming the coating substance should be such that the rinse aid particles are at least substantially water-insoluble. At a temperature of about 30°C, the solubility in water should not exceed about 10 mg/l and preferably should be below 5 mg/l.

30

In any case, however, the coating should preferably have as low a solubility in water as possible, even in water at elevated temperature, in order as far as possible to avoid temperature-independent release of the active substances.

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The principle described above is used for the delayed release of ingredients at a particular point in time in the cleaning operation and may be employed with particular advantage if washing is carried out in the main wash cycle at a relatively low temperature (for example, 55°C), so that the active substance is not released from the rinse aid particles until the rinse cycle at higher temperatures (approximately 70°C).

Preferred particulate rinse aids comprise as coating substance one or more substances having a melting range of between 40°C and 75°C in amounts of from 6 to 30% by weight, preferably from 7.5 to 25% by weight and in particular from 10 to 20% by weight, based in each case on the particle weight, particulate rinse aids being preferred which comprise as ingredient b) one or more substances having a melting range of between 50 and 100°C, preferably between 52.5 and 80°C, and in particular between 55 and 75°C, paraffin waxes having a melting range of from 50°C to 65°C and/or substances from the group of the polyethylene glycols (PEGs) and/or polypropylene glycols (PPGs) being preferred coating substances.

As a third ingredient, the detergent components of the invention comprise one or more fatty substances, with preferred detergent components comprising as ingredient c) from 1 to 60, preferably from 5 to 55, with particular preference from 10 to 50, and in particular from 20 to 45% by weight of fatty substance(s).

In the context of this specification, fatty substances c) are substances which at standard temperature (20°C) are liquid to solid and come from the group of the fatty alcohols, fatty acids and fatty acid derivatives, especially the fatty acid esters. Reaction products of fatty alcohols with alkylene oxides, and the salts of

fatty acids, are included for the purposes of the present specification among the surfactants (see above) and are not fatty substances in the sense of the invention. Fatty substances which may be used with preference in accordance with the invention are fatty alcohols and fatty alcohol mixtures, fatty acids and fatty acid mixtures, fatty acid esters with alkanols and/or diols and/or polyols, fatty acid amides, fatty amines, etc.

Preferred detergent components comprise as ingredient c) one or more substances from the groups of the fatty alcohols, fatty acids, and fatty esters.

Fatty alcohols used are, for example, the alcohols obtainable from natural fats and oils: 1-hexanol (caproyl alcohol), 1-heptanol (enanthyl alcohol), 1-octanol (capryl alcohol), 1-nonanol (pelargonyl alcohol), 1-decanol (capric alcohol), 1-undecanol, 10-undecen-1-ol, 1-dodecanol (lauryl alcohol), 1-tridecanol, 1-tetradecanol (myristyl alcohol), 1-pentadecanol, 1-hexadecanol (cetyl alcohol), 1-heptadecanol, 1-octadecanol (stearyl alcohol), 9-cis-octadecen-1-ol (oleyl alcohol), 9-trans-octadecen-1-ol (elaidyl alcohol), 9-cis-octadecene-1,12-diol (ricinolyl alcohol), all-cis-9,12-octadecadien-1-ol (linoleyl alcohol), all-cis-9,12,15-octadecatrien-1-ol (linolenyl alcohol), 1-nonadecanol, 1-eicosanol (arachidyl alcohol), 9-cis-eicosen-1-ol (gadoleyl alcohol), 5,8,11,14-eicosatetraen-1-ol, 1-heneicosanol, 1-docosanol (behenyl alcohol), 13-cis-docosen-1-ol (erucyl alcohol), 13-trans-docosen-1-ol (brassidyl alcohol), and mixtures of these alcohols. In accordance with the invention, guerbet alcohols and oxo alcohols, for example, C₁₃₋₁₅ oxo alcohols or mixtures of C₁₂₋₁₈ alcohols with C₁₂₋₁₄ alcohols can also be used without problems as fatty substances. However, it is of course also possible to use alcohol mixtures, for example those such as the C₁₆₋₁₈ alcohols prepared by Ziegler

ethylene polymerization. Specific examples of alcohols which may be used as component c) are the alcohols already mentioned above and also lauryl alcohol, palmityl alcohol and stearyl alcohol, and mixtures thereof.

5

Particularly preferred detergent components of the invention comprise as ingredient c) one or more C₁₀₋₃₀ fatty alcohols, preferably C₁₂₋₂₄ fatty alcohols, with particular preference 1-hexadecanol, 1-octadecanol, 10 9-cis-octadecen-1-ol, all-cis-9,12-octadecadien-1-ol, all-cis-9,12,15-octadecatrien-1-ol, 1-docosanol, and mixtures thereof.

As ingredient c) it is also possible to use fatty acids. 15 Industrially, these are obtained primarily from natural fats and oils by hydrolysis. Whereas the alkaline saponification, conducted as long ago as the last century, led directly to the alkali metal salts (soaps), nowadays only water is used industrially to cleave the 20 fats into glycerol and the free fatty acids. Examples of processes employed industrially are cleavage in an autoclave or continuous high-pressure cleavage. Carboxylic acids which may be used as fatty substances in the context of the present invention are, for example, 25 hexanoic acid (caproic acid), heptanoic acid (enanthic acid), octanoic acid (caprylic acid), nonanoic acid (pelargonic acid), decanoic acid (capric acid), undecanoic acid etc. Preference is given in the context of the present invention to the use of fatty acids such 30 as dodecanoic acid (lauric acid), tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), eicosanoic acid (arachidic acid), docosanoic acid (behenic acid), tetracosanoic acid (lignoceric acid), hexacosanoic acid (cerotic acid), triacontanoic acid (melissic acid) and 35 also the unsaturated species 9c-hexadecenoic acid (palmitoleic acid), 6c-octadecenoic acid (petroselinic

acid), 6t-octadecenoic acid (petroselaidic acid), 9c-octadecenoic acid (oleic acid), 9t-octadecenoic acid (elaidic acid), 9c,12c-octadecadienoic acid (linoleic acid), 9t,12t-octadecadienoic acid (linolaidic acid), and 9c,12c,15c-octadecatrienoic acid (linolenic acid). Also possible for use, of course, are tridecanoic acid, pentadecanoic acid, margaric acid, nonadecanoic acid, erucic acid, eleostearic acid, and arachidonic acid. For reasons of cost it is preferred to use not the pure species but rather technical-grade mixtures of the individual acids as obtainable from fat cleavage. Such mixtures are, for example, coconut oil fatty acid (approximately 6% by weight C_8 , 6% by weight C_{10} , 48% by weight C_{12} , 18% by weight C_{14} , 10% by weight C_{16} , 2% by weight C_{18} , 8% by weight $C_{18\cdot}$, 1% by weight $C_{18\cdots}$), palm kernel oil fatty acid (approximately 4% by weight C_8 , 5% by weight C_{10} , 50% by weight C_{12} , 15% by weight C_{14} , 7% by weight C_{16} , 2% by weight C_{18} , 15% by weight $C_{18\cdot}$, 1% by weight $C_{18\cdots}$), tallow fatty acid (approximately 3% by weight C_{14} , 26% by weight C_{16} , 2% by weight $C_{16\cdot}$, 2% by weight C_{17} , 17% by weight C_{18} , 44% by weight $C_{18\cdot}$, 3% by weight $C_{18\cdots}$, 1% by weight $C_{18\cdots\cdots}$), hardened tallow fatty acid (approximately 2% by weight C_{14} , 28% by weight C_{16} , 2% by weight C_{17} , 63% by weight C_{18} , 1% by weight $C_{18\cdot}$), technical-grade oleic acid (approximately 1% by weight C_{12} , 3% by weight C_{14} , 5% by weight C_{16} , 6% by weight $C_{16\cdot}$, 1% by weight C_{17} , 2% by weight C_{18} , 70% by weight $C_{18\cdot}$, 10% by weight $C_{18\cdots}$, 0.5% by weight $C_{18\cdots\cdots}$), technical-grade palmitic/stearic acid (approximately 1% by weight C_{12} , 2% by weight C_{14} , 45% by weight C_{16} , 2% by weight C_{17} , 47% by weight C_{18} , 1% by weight $C_{18\cdot}$), and soybean oil fatty acid (approximately 2% by weight C_{14} , 15% by weight C_{16} , 5% by weight C_{18} , 25% by weight $C_{18\cdot}$, 45% by weight $C_{18\cdots}$, 7% by weight $C_{18\cdots\cdots}$).

As fatty acid esters, use may be made of the esters of fatty acids with alkanols, diols or polyols, fatty acid

polyol esters being preferred. Suitable fatty acid polyol esters include monoesters and diesters of fatty acids with certain polyols. The fatty acids that are esterified with the polyols are preferably saturated or unsaturated fatty acids of 12 to 18 carbon atoms, examples being lauric acid, myristic acid, palmitic acid, and stearic acid, preference being given to the use of the fatty acid mixtures obtained industrially, for example, the acid mixtures derived from coconut oil, palm kernel oil or tallow fat. In particular, acids or mixture of acids having 16 to 18 carbon atoms, such as tallow fatty acid, for example, are suitable for esterification with the polyhydric alcohols. In the context of the present invention, suitable polyols for esterification with the aforementioned fatty acids include sorbitol, trimethylolpropane, neopentyl glycol, ethylene glycol, polyethylene glycols, glycerol, and polyglycerols.

Preferred embodiments of the present invention provide for the polyol esterified with fatty acid(s) to be glycerol. Accordingly, preference is given to detergent components of the invention comprising as ingredient c) one or more fatty substances from the group consisting of fatty alcohols and fatty acid glycerides. Particularly preferred detergent components comprise as component c) a fatty substance from the group consisting of the fatty alcohols and fatty acid monoglycerides. Examples of such fatty substances used with preference are glyceryl monostearate and glyceryl monopalmitate.

The particulate rinse aids of the invention may preferably comprise as ingredient d) further active substances and/or auxiliaries from the groups of the surfactants, bleaches, bleach activators, soil release polymers, enzymes, silver protectants, complexing agents, dyes and fragrances in amounts of from 0 to 50% by weight, preferably from 2.5 to 45% by weight, with

particular preference from 5 to 40% by weight, and in particular from 10 to 30% by weight.

5 Particular preference is given in this case to the use of the surfactants described earlier on above, so that preferred particulate rinse aids further comprise as ingredient d) surfactant(s), preferably nonionic surfactant(s), with particular preference those from the group of the alkoxyated alcohols, in amounts of from 5
10 to 47.5% by weight, preferably from 10 to 45% by weight, with particular preference from 15 to 42.5% by weight, and in particular from 20 to 40% by weight, based in each case on the particulate rinse aid.

15 The other detergent ingredients which may be incorporated as component d) into the rinse aids of the invention are described in detail later on below.

20 As ingredient e), the particulate rinse aids of the invention comprise diquaternalary polysiloxanes, the abovementioned remarks concerning preferred species continuing to apply in their entirety. In order to avoid redundancy, therefore, reference is made to the formulae given above. Preferred particulate rinse aids comprise
25 diquaternalary polysiloxanes, preferably diquaternalary polysiloxanes of the formula I, with particular preference diquaternalary poly(dimethyl-siloxanes) of the formula II, and in particular diquaternalary poly(dimethylsiloxanes) of the formula III, in amounts of
30 from 0.5 to 60% by weight, preferably from 1 to 50% by weight, with particular preference from 2.5 to 40% by weight, and in particular from 5 to 30% by weight, based in each case on the particulate rinse aid.

35 The present invention additionally provides a process for preparing particulate detergent components, which comprises applying a melt comprising

- a) from 30 to 70% by weight of coating substance(s) having a melting point above 50°C,
- b) from 0 to 65% by weight of fatty substance(s),
- c) from 0 to 50% by weight of further active substances and/or auxiliaries, and
- d) from 0.1 to 70% by weight of diquaternary polysiloxanes

to one or more support materials and shaping the mixture.

10 In this process variant, first of all a melt is prepared, which may include further active substances and auxiliaries. This melt is applied to a support material and shaped as a mixture with said support material.

15 With the abovementioned preparation process for the rinse aid particles of the invention, preferred process variants are those wherein the meltable substance accounts for from 25 to 85% by weight, preferably from 30 to 70% by weight, and in particular from 40 to 50% by weight of the melt.

20 The application of the melt to the support material may be conducted in all customary mixing equipment. The shaping step for the mixture of melt and support material is likewise not subject to any technical restriction, so that here as well the skilled worker is able to select from the processes customary to him or her. In the course of experiments conducted by the applicant, processes which have proven preferable are those wherein the shaping takes place by granulating, compacting, pelletizing, extruding, or tableting.

30 The process of the invention embraces the application of melts comprising the ingredients a) to d) to support materials. In principle, melt and support material(s) may be present in varying amounts in the resultant rinse aid particles. In preferred processes, the mixture shaped

comprises from 5 to 50% by weight, preferably from 10 to 45% by weight, with particular preference from 15 to 40% by weight, and in particular from 20 to 35% by weight of a melt comprising the ingredients a) to d), and from 50 to 95% by weight, preferably from 55 to 90% by weight, with particular preference from 60 to 85% by weight, and in particular from 65 to 80% by weight, of support material(s).

Regarding the ingredients which are used in the process of the invention and are processed to the support material-based detergent components of the invention, the comments made earlier on above apply analogously.

The detergent components of the invention may also be formulated without support material, so that they consist solely of the ingredients a) to d). In this case, for the preparation of particulate detergent components of the invention, prilling, pelletizing and flaking by means of cooling rolls have proven particularly suitable.

The present invention therefore additionally provides, in a first embodiment, a process for preparing prilled detergent components, which comprises spraying a melt comprising

- a) from 30 to 70% by weight of coating substance(s) having a melting point above 50°C,
 - b) from 0 to 65% by weight of fatty substance(s),
 - c) from 0 to 50% by weight of further active substances and/or auxiliaries, and
 - d) from 0.1 to 70% by weight of diquaternary polysiloxanes
- into a cold gas stream.

The process of the invention, which is referred to for short as prilling, comprises the production of granular elements from meltable substances, the melt comprising

the ingredients a) to d) being sprayed in defined droplet size at the top of a tower, solidifying in free fall, and being obtained as prill granules at the base of the tower.

5

As the cold gas stream it is possible in very general terms to use all gases, the temperature of the gas being below the melting temperature of the melt. In order to avoid long falling sections, use is frequently made of cooled gases, for example, supercooled air or even liquid nitrogen, which is injected through a nozzle into the spray towers.

10

The particle size of the resulting prills may be varied by way of the choice of droplet size, with particle sizes which are easy to realize technically lying within the range from 0.5 to 2 mm, preferably around 1 mm.

15

An alternative process to prilling is pelletizing. A further embodiment of the present invention therefore envisages a process for preparing pelletized detergent components, which comprises metering a melt comprising

20

- a) from 30 to 70% by weight of coating substance(s) having a melting point above 50°C,
- 25 b) from 0 to 65% by weight of fatty substance(s),
- c) from 0 to 50% by weight of further active substances and/or auxiliaries, and
- d) from 0.1 to 70% by weight of diquatarnary polysiloxanes

25

30 onto cooled pelletizing plates.

Pelletizing comprises the metering of the melt comprising the ingredients a) to d) onto rotating, inclined plates which have a temperature below the melting temperature of the melt and are preferably cooled to below room temperature. Here again, process variants may be practiced in which the pelletizing plates are

35

supercooled. In this case, however, measures must be taken to counter the condensation of atmospheric moisture.

- 5 Pelletizing produces relatively large particles, which in standard industrial processes have sizes of between 2 and 10 mm, preferably between 3 and 6 mm.

10 As an even more cost-effective variant for producing particulate detergent components of the stated composition from melts, the use of cooling rolls is appropriate. A further subject of the present invention is therefore a process for preparing particulate detergent components, which comprises applying a melt
15 comprising

- a) from 30 to 70% by weight of coating substance(s) having a melting point above 50°C,
- b) from 0 to 65% by weight of fatty substance(s),
- c) from 0 to 50% by weight of further active
20 substances and/or auxiliaries, and
- d) from 0.1 to 70% by weight of diquaternary polysiloxanes

by spraying or otherwise to a cooling roll, scraping off the solidified melt, and comminuting the scrapings if
25 necessary.

The use of cooling rolls permits ready establishment of the desired particle size range, which in this process of the invention may also be below 1 mm, for example from
30 200 to 700 μm .

The rinse aid particles of the invention may be given directly to the consumer, who then doses them into the detergent additionally as required. On the basis of this
35 additional dosing step, however, apart from the solid supply form and the addition to the same dispenser, the advantages relative to liquid rinse aid compositions

would be minimized. It is therefore preferred to admix the rinse aid particles of the invention to particulate machine dishwashing compositions.

5 The present invention therefore additionally provides a particulate machine dishwashing composition comprising builders and also, optionally, further ingredients from the groups of the surfactants, enzymes, bleaches, bleach
10 activators, corrosion inhibitors, polymers, dyes, and fragrances, which comprises a particulate rinse aid of the invention in amounts of from 0.5 to 30% by weight, preferably from 1 to 25% by weight, and in particular from 5 to 15% by weight, based in each case on overall composition.

15 The ingredients of the machine dishwashing compositions are described hereinbelow. In some cases, they may also be present as active substances or support materials in the rinse aid particles of the invention.

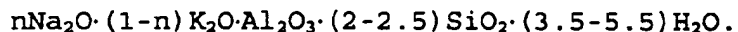
20 The most important ingredients of machine dishwashing compositions are builders. The machine dishwashing detergents of the invention may comprise all of the builders commonly used in detergents, i.e., in
25 particular, zeolites, silicates, carbonates, organic cobuilders, and - where there are no ecological prejudices against their use - the phosphates as well. The builders mentioned below are all suitable as support materials for the rinse aid particles of the invention,
30 as set out earlier on above.

Suitable crystalline, layered sodium silicates possess the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$, where M is sodium or hydrogen, x is a number from 1.9 to 4, y is a number from
35 0 to 20, and preferred values for x are 2, 3 or 4. Crystalline phyllosilicates of this kind are described, for example, in European Patent Application

EP-A-0 164 514. Preferred crystalline phyllosilicates of the formula indicated are those in which M is sodium and x adopts the value 2 or 3. In particular, both β - and δ -sodium disilicates $\text{Na}_2\text{Si}_2\text{O}_5 \cdot y\text{H}_2\text{O}$ are preferred, β -sodium disilicate, for example, being obtainable by the process described in International Patent Application WO-A-91/08171.

It is also possible to use amorphous sodium silicates having an $\text{Na}_2\text{O}:\text{SiO}_2$ modulus of from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8, and in particular from 1:2 to 1:2.6, which are dissolution-retarded and have secondary washing properties. The retardation of dissolution relative to conventional amorphous sodium silicates may have been brought about in a variety of ways - for example, by surface treatment, compounding, compacting, or overdrying. In the context of this invention, the term "amorphous" also embraces "X-ray-amorphous". This means that in X-ray diffraction experiments the silicates do not yield the sharp X-ray reflections typical of crystalline substances but instead yield at best one or more maxima of the scattered X-radiation, having a width of several degree units of the diffraction angle. However, even particularly good builder properties may result if the silicate particles in electron diffraction experiments yield vague or even sharp diffraction maxima. The interpretation of this is that the products have microcrystalline regions with a size of from 10 to several hundred nm, values up to max. 50 nm and in particular up to max. 20 nm being preferred. So-called X-ray-amorphous silicates of this kind, which likewise possess retarded dissolution relative to the conventional waterglasses, are described, for example, in German Patent Application DE-A-44 00 024. Particular preference is given to compacted amorphous silicates, compounded amorphous silicates, and overdried X-ray-amorphous silicates.

The finely crystalline, synthetic zeolite used, containing bound water, is preferably zeolite A and/or P. A particularly preferred zeolite P is Zeolite MAP® (commercial product from Crosfield). Also suitable, however, are zeolite X and also mixtures of A, X and/or P. Another product available commercially and able to be used with preference in the context of the present invention, for example, is a cocrystallizate of zeolite X and zeolite A (approximately 80% by weight zeolite X), which is sold by CONDEA Augusta S.p.A. under the brand name VEGOBOND AX® and may be described by the formula



Suitable zeolites have an average particle size of less than 10 μm (volume distribution; measurement method: Coulter counter) and contain preferably from 18 to 22% by weight, in particular from 20 to 22% by weight, of bound water.

Of course, the widely known phosphates may also be used as builder substances provided such a use is not to be avoided on ecological grounds. Among the large number of commercially available phosphates, the alkali metal phosphates, with particular preference being given to pentasodium and pentapotassium triphosphate (sodium and potassium tripolyphosphate, respectively), possess the greatest importance in the detergents industry.

Alkali metal phosphates is the collective term for the alkali metal (especially sodium and potassium) salts of the various phosphoric acids, among which metaphosphoric acids $(\text{HPO}_3)_n$ and orthophosphoric acid H_3PO_4 , in addition to higher-molecular-mass representatives, may be distinguished. The phosphates combine a number of advantages: they act as alkali carriers, prevent

limescale deposits on machine components, and lime encrustations on fabrics, and additionally contribute to cleaning performance.

5 Sodium dihydrogen phosphate, NaH_2PO_4 , exists as the dihydrate (density 1.91 g cm^{-3} , melting point 60°) and as the monohydrate (density 2.04 g cm^{-3}). Both salts are white powders of very ready solubility in water which
 10 lose the water of crystallization on heating and undergo conversion at 200°C into the weakly acidic diphosphate (disodium dihydrogen diphosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$) and at a higher temperature into sodium trimetaphosphate ($\text{Na}_3\text{P}_3\text{O}_9$) and Maddrell's salt (see below). NaH_2PO_4 reacts acidically; it is formed if phosphoric acid is adjusted
 15 to a pH of 4.5 using sodium hydroxide solution and the slurry is sprayed. Potassium dihydrogen phosphate (primary or monobasic potassium phosphate, potassium biphosphate, PDP), KH_2PO_4 , is a white salt with a density of 2.33 g cm^{-3} , has a melting point of 253° [decomposition with formation of potassium polyphosphate (KPO_3)_x], and is
 20 readily soluble in water.

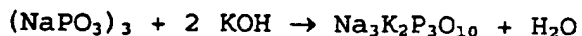
Disodium hydrogen phosphate (secondary sodium phosphate), Na_2HPO_4 , is a colorless, crystalline salt which is very
 25 readily soluble in water. It exists in anhydrous form and with 2 mol (density 2.066 g cm^{-3} , water loss at 95°), 7 mol (density 1.68 g cm^{-3} , melting point 48° with loss of 5 H_2O), and 12 mol (density 1.52 g cm^{-3} , melting point 35° with loss of 5 H_2O) of water, becomes anhydrous at 100° ,
 30 and if heated more intensely undergoes transition to the diphosphate $\text{Na}_4\text{P}_2\text{O}_7$. Disodium hydrogen phosphate is prepared by neutralizing phosphoric acid with sodium carbonate solution using phenolphthalein as indicator. Dipotassium hydrogen phosphate (secondary or dibasic
 35 potassium phosphate), K_2HPO_4 , is an amorphous white salt which is readily soluble in water.

Trisodium phosphate, tertiary sodium phosphate, Na_3PO_4 , exists as colorless crystals which as the dodecahydrate have a density of 1.62 g cm^{-3} and a melting point of $73-76^\circ\text{C}$ (decomposition), as the decahydrate (corresponding to 19-20% P_2O_5) have a melting point of 100°C , and in anhydrous form (corresponding to 39-40% P_2O_5) have a density of 2.536 g cm^{-3} . Trisodium phosphate is readily soluble in water, with an alkaline reaction, and is prepared by evaporative concentration of a solution of precisely 1 mol of disodium phosphate and 1 mol of NaOH. Tripotassium phosphate (tertiary or tribasic potassium phosphate), K_3PO_4 , is a white, deliquescent, granular powder of density 2.56 g cm^{-3} , has a melting point of 1340° , and is readily soluble in water with an alkaline reaction. It is produced, for example, when Thomas slag is heated with charcoal and potassium sulfate. Despite the relatively high price, the more readily soluble and therefore highly active potassium phosphates are frequently preferred in the detergents industry over the corresponding sodium compounds.

Tetrasodium diphosphate (sodium pyrophosphate), $\text{Na}_4\text{P}_2\text{O}_7$, exists in anhydrous form (density 2.534 g cm^{-3} , melting point 988° , 880° also reported) and as the decahydrate (density $1.815-1.836 \text{ g cm}^{-3}$, melting point 94° with loss of water). Both substances are colorless crystals which dissolve in water with an alkaline reaction. $\text{Na}_4\text{P}_2\text{O}_7$ is formed when disodium phosphate is heated to $> 200^\circ$ or by reacting phosphoric acid with sodium carbonate in stoichiometric ratio and dewatering the solution by spraying. The decahydrate complexes heavy metal salts and water hardeners and therefore reduces the hardness of the water. Potassium diphosphate (potassium pyrophosphate), $\text{K}_4\text{P}_2\text{O}_7$, exists in the form of the trihydrate and is a colorless, hygroscopic powder of density 2.33 g cm^{-3} which is soluble in water, the pH of the 1% strength solution at 25° being 10.4.

Condensation of NaH_2PO_4 or of KH_2PO_4 gives rise to higher-molecular-mass sodium and potassium phosphates, among which it is possible to distinguish cyclic representatives, the sodium and potassium metaphosphates, and catenated types, the sodium and potassium polyphosphates. For the latter in particular a large number of names are in use: fused or calcined phosphates, Graham's salt, Kurrol's and Maddrell's salt. All higher sodium and potassium phosphates are referred to collectively as condensed phosphates.

The industrially important pentasodium triphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$ (sodium tripolyphosphate), is a nonhygroscopic, white, water-soluble salt which is anhydrous or crystallizes with 6 H_2O and has the general formula $\text{NaO}[\text{P}(\text{O})(\text{ONa})-\text{O}]_n-\text{Na}$ where $n = 3$. About 17 g of the anhydrous salt dissolve in 100 g of water at room temperature, about 20 g at 60° , around 32 g at 100° ; after heating the solution at 100°C for two hours, about 8% orthophosphate and 15% diphosphate are produced by hydrolysis. For the preparation of pentasodium triphosphate, phosphoric acid is reacted with sodium carbonate solution or sodium hydroxide solution in stoichiometric ratio and the solution is dewatered by spraying. In a similar way to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves numerous insoluble metal compounds (including lime soaps, etc.). Pentapotassium triphosphate, $\text{K}_5\text{P}_3\text{O}_{10}$ (potassium tripolyphosphate), is commercialized, for example, in the form of a 50% strength by weight solution ($> 23\% \text{P}_2\text{O}_5$, $25\% \text{K}_2\text{O}$). The potassium polyphosphates find broad application in the detergents industry. There also exist sodium potassium tripolyphosphates, which may likewise be used for the purposes of the present invention. These are formed, for example, when sodium trimetaphosphate is hydrolyzed with KOH :



5 They can be used in accordance with the invention in
precisely the same way as sodium tripolyphosphate,
potassium tripolyphosphate, or mixtures of these two;
mixtures of sodium tripolyphosphate and sodium potassium
tripolyphosphate, or mixtures of potassium
tripolyphosphate and sodium potassium tripolyphosphate,
10 or mixtures of sodium tripolyphosphate and potassium
tripolyphosphate and sodium potassium tripolyphosphate,
may also be used in accordance with the invention.

15 Organic cobuilders which may be used in the machine
dishwashing compositions of the invention are, in
particular, polycarboxylates/polycarboxylic acids,
polymeric polycarboxylates, aspartic acid, polyacetals,
dextrins, further organic cobuilders (see below), and
phosphonates. These classes of substance are described
20 below.

Organic builder substances which may be used are, for
example, the polycarboxylic acids usable in the form of
their sodium salts, the term polycarboxylic acids meaning
25 those carboxylic acids which carry more than one acid
function. Examples of these are citric acid, adipic acid,
succinic acid, glutaric acid, malic acid, tartaric acid,
maleic acid, fumaric acid, sugar acids, amino carboxylic
acids, nitrilotriacetic acid (NTA), provided such use is
30 not objectionable on ecological grounds, and also
mixtures thereof. Preferred salts are the salts of the
polycarboxylic acids such as citric acid, adipic acid,
succinic acid, glutaric acid, tartaric acid, sugar acids,
and mixtures thereof.

35

The acids per se may also be used. In addition to their
builder effect, the acids typically also possess the

property of an acidifying component and thus also serve to establish a lower and milder pH of detergents. In this context, mention may be made in particular of citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid, and any desired mixtures thereof.

Also suitable as builders are polymeric polycarboxylates; these are, for example, the alkali metal salts of polyacrylic acid or of polymethacrylic acid, examples being those having a relative molecular mass of from 500 to 70,000 g/mol.

The molecular masses reported for polymeric polycarboxylates, for the purposes of this document, are weight-average molecular masses, M_w , of the respective acid form, determined basically by means of gel permeation chromatography (GPC) using a UV detector. The measurement was made against an external polyacrylic acid standard, which owing to its structural similarity to the polymers under investigation provides realistic molecular weight values. These figures differ markedly from the molecular weight values obtained using polystyrenesulfonic acids as the standard. The molecular masses measured against polystyrenesulfonic acids are generally much higher than the molecular masses reported in this document.

Suitable polymers are, in particular, polyacrylates, which preferably have a molecular mass of from 2000 to 20,000 g/mol. Owing to their superior solubility, preference in this group may be given in turn to the short-chain polyacrylates, which have molecular masses of from 2000 to 10,000 g/mol, and with particular preference from 3000 to 5000 g/mol.

Also suitable are copolymeric polycarboxylates, especially those of acrylic acid with methacrylic acid

and of acrylic acid or methacrylic acid with maleic acid. Copolymers which have been found particularly suitable are those of acrylic acid with maleic acid which contain from 50 to 90% by weight of acrylic acid and from 50 to 10% by weight of maleic acid. Their relative molecular mass, based on free acids, is generally from 2000 to 70,000 g/mol, preferably from 20,000 to 50,000 g/mol, and in particular from 30,000 to 40,000 g/mol.

The (co)polymeric polycarboxylates can be used either as powders or as aqueous solutions. The (co)polymeric polycarboxylate content of the compositions is preferably from 0.5 to 20% by weight, in particular from 3 to 10% by weight.

In order to improve the solubility in water, the polymers may also contain allylsulfonic acids, such as allyloxybenzenesulfonic acid and methallylsulfonic acid, for example, as monomers.

Particular preference is also given to biodegradable polymers comprising more than two different monomer units, examples being those comprising, as monomers, salts of acrylic acid and of maleic acid, and also vinyl alcohol or vinyl alcohol derivatives, or those comprising, as monomers, salts of acrylic acid and of 2-alkylallylsulfonic acid, and also sugar derivatives.

Further preferred copolymers are those whose monomers are preferably acrolein and acrylic acid salts, and, respectively acrolein and vinyl acetate.

Similarly, further preferred builder substances that may be mentioned include polymeric amino dicarboxylic acids, their salts or their precursor substances. Particular preference is given to polyaspartic acids and their salts

and derivatives, which have not only cobuilder properties but also a bleach-stabilizing action.

5 Further suitable builder substances are polyacetals, which may be obtained by reacting dialdehydes with polyol
carboxylic acids having 5 to 7 carbon atoms and at least
3 hydroxyl groups. Preferred polyacetals are obtained
from dialdehydes such as glyoxal, glutaraldehyde,
10 terephthalaldehyde and mixtures thereof and from polyol
carboxylic acids such as gluconic acid and/or
glucoheptonic acid.

Further suitable organic builder substances are dextrans, examples being oligomers and polymers of carbohydrates,
15 which may be obtained by partial hydrolysis of starches. The hydrolysis can be conducted by customary processes, for example, acid-catalyzed or enzyme-catalyzed processes. The hydrolysis products preferably have average molecular masses in the range from 400 to 500,000
20 g/mol. Preference is given here to a polysaccharide having a dextrose equivalent (DE) in the range from 0.5 to 40, in particular from 2 to 30, DE being a common measure of the reducing effect of a polysaccharide in comparison to dextrose, which possesses a DE of 100. It
25 is possible to use both maltodextrans having a DE of between 3 and 20 and dried glucose syrups having a DE of between 20 and 37, and also so-called yellow dextrans and white dextrans having higher molecular masses, in the range from 2000 to 30,000 g/mol.

30 The oxidized derivatives of such dextrans comprise their products of reaction with oxidizing agents which are able to oxidize at least one alcohol function of the saccharide ring to the carboxylic acid function. A
35 product oxidized at C₆ of the saccharide ring may be particularly advantageous.

Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are further suitable cobuilders. Ethylenediamine N,N'-disuccinate (EDDS) is used preferably in the form of its sodium or
5 magnesium salts. Further preference in this context is given to glycerol disuccinates and glycerol trisuccinates as well. Suitable use amounts in formulations containing zeolite and/or silicate are from 3 to 15% by weight.

10 Examples of further useful organic cobuilders are acetylated hydroxy carboxylic acids and their salts, which may also, if desired, be present in lactone form and which contain at least 4 carbon atoms, at least one hydroxyl group, and not more than two acid groups.

15 A further class of substance having cobuilder properties is represented by the phosphonates. The phosphonates in question are, in particular, hydroxyalkane- and aminoalkanephosphonates. Among the
20 hydroxyalkanephosphonates, 1-hydroxyethane-1,1-diphosphate (HEDP) is of particular importance as a cobuilder. It is used preferably as the sodium salt, the disodium salt being neutral and the tetrasodium salt giving an alkaline (pH 9) reaction. Suitable
25 aminoalkanephosphonates are preferably ethylenediamine-tetramethylenephosphonate (EDTMP), diethylenetriamine-pentamethylenephosphonate (DTPMP), and their higher homologs. They are used preferably in the form of the neutrally reacting sodium salts, e.g., as the hexasodium
30 salt of EDTMP or as the hepta- and octa-sodium salt of DTPMP. As a builder in this case, preference is given to using HEDP from the class of the phosphonates. Furthermore, the aminoalkanephosphonates possess a pronounced heavy metal binding capacity. Accordingly, and
35 especially if the compositions also contain bleach, it may be preferred to use aminoalkanephosphonates,

especially DTPMP, or to use mixtures of said phosphonates.

Furthermore, all compounds capable of forming complexes
5 with alkaline earth metal ions may be used as cobuilders.

Important ingredients of detergents in addition to the
builders are, in particular, substances from the groups
of the surfactants (see above), bleaches, bleach
10 activators, enzymes, polymers, fragrances, and dyes.
Important representatives from the aforementioned classes
of substance are described below.

Among the compounds used as bleaches which yield H_2O_2 in
15 water, particular importance is possessed by sodium
perborate tetrahydrate and sodium perborate monohydrate.
Examples of further bleaches which may be used are sodium
percarbonate, peroxy pyrophosphates, citrate perhydrates,
and also H_2O_2 -donating peracidic salts or peracids, such
20 as perbenzoates, peroxophthalates, diperazelaic acid,
phthaloimino peracid, or diperdodecanedioic acid.
Detergents of the invention may also comprise bleaches
from the group of organic bleaches. Typical organic
bleaches are the diacyl peroxides, such as dibenzoyl
25 peroxide, for example. Further typical organic bleaches
are the peroxy acids, particular examples being the alkyl
peroxy acids and the aryl peroxy acids. Preferred
representatives are (a) peroxybenzoic acid and its ring-
substituted derivatives, such as alkylperoxybenzoic
30 acids, but also peroxy- α -naphthoic acid and magnesium
monoperphthalate, (b) aliphatic or substituted aliphatic
peroxy acids, such as peroxy lauric acid, peroxy stearic
acid, ϵ -phthalimidoperoxy caproic acid
[phthaloiminoperoxyhexanoic acid (PAP)], o-
35 carboxybenzamidoperoxy caproic acid, N-
nonenylamidoperadipic acid and N-nonenylamido-
persuccinates, and (c) aliphatic and araliphatic peroxy

dicarboxylic acids, such as 1,12-diperoxydecane-dicarboxylic acid, 1,9-diperoxyazelaic acid, diperoxy-sebacic acid, diperoxybrassylic acid, the diperoxy-phthalic acids, 2-decyldiperoxybutane-1,4-dioic acid and
 5 N,N-terephthaloyldi(6-aminopercaproic acid) may also be used.

Bleaches in the detergents of the invention for machine dishwashing may also be substances which release chlorine
 10 or bromine. Among the suitable chlorine- or bromine-releasing materials examples include heterocyclic N-bromoamides and N-chloroamides, examples being trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid and/or dichloroisocyanuric acid
 15 (DICA) and/or salts thereof with cations such as potassium and sodium. Hydantoin compounds, such as 1,3-dichloro-5,5-dimethylhydantoin, are likewise suitable.

In order to achieve an "after-bleaching" effect in the
 20 rinse cycle, the abovementioned bleaches may also be introduced into the machine dishwashing compositions of the invention in whole or in part by way of the rinse aid particles.

Bleach activators, which boost the action of the
 25 bleaches, were mentioned earlier on above as a possible ingredient of the rinse aid particles. Known bleach activators are compounds containing one or more N-acyl and/or O-acyl groups, such as substances from the class
 30 of the anhydrides, esters, imides and acylated imidazoles or oximes. Examples are tetraacetythylenediamine TAED, tetraacetylmethylene-diamine TAMd, and tetraacetylhexylenediamine TAHD, and also
 35 pentaacetylglucose PAG, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine DADHT, and isatoic anhydride ISA.

Bleach activators which may be used are compounds which under perhydrolysis conditions give rise to aliphatic peroxy carboxylic acids having preferably 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or substituted or unsubstituted perbenzoic acid. Suitable substances are those which carry O-acyl and/or N-acyl groups of the stated number of carbon atoms, and/or substituted or unsubstituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylenediamine (TAED), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N-acylimides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, especially phthalic anhydride, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran, N-methylmorpholiniumacetone nitrile methyl sulfate (MMA), and the enol esters known from German Patent Applications DE 196 16 693 and DE 196 16 767, and also acetylated sorbitol and mannitol and/or mixtures thereof (SORMAN), acylated sugar derivatives, especially pentaacetylglucose (PAG), pentaacetylfructose, tetraacetylxylose and octaacetyllactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example, N-benzoylcaprolactam. Hydrophilically substituted acylacetals and acyllactams are likewise used with preference. Combinations of conventional bleach activators may also be used.

In addition to the conventional bleach activators, or instead of them, it is also possible to incorporate what are known as bleaching catalysts into the rinse aid particles. These substances are bleach-boosting transition metal salts or transition metal complexes such

as, for example, Mn-, Fe-, Co-, Ru- or Mo-salen complexes or -carbonyl complexes. Other bleaching catalysts which can be used include Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes with N-containing tripod ligands, and also Co-,
 5 Fe-, Cu- and Ru-ammine complexes.

Preference is given to the use of bleach activators from the group of polyacylated alkylenediamines, especially tetraacetythylenediamine (TAED), N-acyl imides,
 10 especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoxybenzenesulfonate (n- or iso-NOBS), N-methylmorpholiniumacetonitrile methyl sulfate (MMA), preferably in amounts of up to 10% by weight, in
 15 particular from 0.1% by weight to 8% by weight, more particularly from 2 to 8% by weight, and with particular preference from 2 to 6% by weight, based on the overall composition.

20 Bleach-boosting transition metal complexes, especially those with the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, preferably selected from the group of manganese and/or cobalt salts and/or complexes, with particular preference from cobalt ammine complexes,
 25 cobalt acetato complexes, cobalt carbonyl complexes, the chlorides of cobalt or manganese, and manganese sulfate, are used in customary amounts, preferably in an amount of up to 5% by weight, in particular from 0.0025% by weight to 1% by weight, and with particular preference from
 30 0.01% by weight to 0.25% by weight, based in each case on the overall composition. In specific cases, however, it is also possible to use a greater amount of bleach activator.

35 Suitable enzymes in the detergents of the invention include in particular those from the classes of the hydrolases such as the proteases, esterases, lipases or

lipolytic enzymes, amylases, glycosyl hydrolases, and mixtures of said enzymes. All of these hydrolases contribute to removing stains, such as proteinaceous, fatty or starchy marks. For bleaching, it is also possible to use oxidoreductases. Especially suitable enzymatic active substances are those obtained from bacterial strains or fungi such as *Bacillus subtilis*, *Bacillus licheniformis*, *Streptomyces griseus*, *Coprinus cinereus* and *Humicola insolens*, and also from genetically modified variants thereof. Preference is given to the use of proteases of the subtilisin type, and especially to proteases obtained from *Bacillus lentus*. Of particular interest in this context are enzyme mixtures, examples being those of protease and amylase or protease and lipase or lipolytic enzymes, or of protease, amylase and lipase or lipolytic enzymes, or protease, lipase or lipolytic enzymes, but especially protease and/or lipase-containing mixtures or mixtures with lipolytic enzymes. Examples of such lipolytic enzymes are the known cutinases. Peroxidases or oxidases have also proven suitable in some cases. The suitable amylases include, in particular, alpha-amylases, iso-amylases, pullulanases, and pectinases.

The enzymes may be adsorbed on carrier substances or embedded in coating substances in order to protect them against premature decomposition. The proportion of the enzymes, enzyme mixtures or enzyme granules may be, for example, from about 0.1 to 5% by weight, preferably from 0.5 to about 4.5% by weight.

Dyes and fragrances may be added to the machine dishwashing compositions of the invention in order to enhance the esthetic appeal of the products which are formed and to provide the consumer with not only the performance but also a visually and sensorially "typical and unmistakable" product. As perfume oils and/or

fragrances it is possible to use individual odorant compounds, examples being the synthetic products of the ester, ether, aldehyde, ketone, alcohol, and hydrocarbon types. Odorant compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethyl methylphenylglycinate, allyl cyclo-hexylpropionate, styryl propionate, and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having 8-18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for example, the ionones, α -isomethylionone and methyl cedryl ketone; the alcohols include anethole, citronellol, eugenol, geraniol, linalool, phenylethyl alcohol, and terpineol; the hydrocarbons include primarily the terpenes such as limonene and pinene. Preference, however, is given to the use of mixtures of different odorants, which together produce an appealing fragrance note. Such perfume oils may also contain natural odorant mixtures, as obtainable from plant sources, examples being pine oil, citrus oil, jasmine oil, patchouli oil, rose oil or ylang-ylang oil. Likewise suitable are clary sage oil, camomile oil, clove oil, balm oil, mint oil, cinnamon leaf oil, lime blossom oil, juniperberry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil, and also orange blossom oil, neroli oil, orange peel oil, and sandalwood oil.

The fragrances may be incorporated directly into the detergents of the invention; alternatively, it may be advantageous to apply the fragrances to supports, which strengthen the adherence of the perfume to the laundry and, by slowing the release of fragrance, provide for

long-lasting fragrance of the textiles. Materials which have become established as such supports are, for example, cyclodextrins, it being possible in addition for the cyclodextrin-perfume complexes to be additionally coated with further auxiliaries. Incorporating the fragrances into the rinse aid particles of the invention is also possible, and results in a fragrance sensation when the machine is opened (see above).

In order to enhance the esthetic appeal of the compositions produced in accordance with the invention, they (or parts thereof) may be colored with appropriate dyes. Preferred dyes, whose selection presents no difficulty whatsoever to the skilled worker, possess a high level of storage stability and insensitivity to the other ingredients of the compositions or to light and possess no pronounced affinity for the substrates to be treated with the compositions, such as glass, ceramic, or plasticware, so as not to stain them.

The detergents of the invention may include corrosion inhibitors for protecting the ware or the machine, with special importance in the field of machine dishwashing being possessed, in particular, by silver protectants. The known substances of the prior art may be used. In general it is possible to use, in particular, silver protectants selected from the group consisting of triazoles, benzotriazoles, bisbenzotriazoles, amino-triazoles, alkylaminotriazoles, and transition metal salts or transition metal complexes. Particular preference is given to the use of benzotriazole and/or alkylaminotriazole. Frequently encountered in cleaning formulations, furthermore, are agents containing active chlorine, which may significantly reduce corrosion of the silver surface. In chlorine-free cleaners, use is made in particular of oxygen-containing and nitrogen-containing organic redox-active compounds, such as divalent and

trivalent phenols, e.g. hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucinol, pyrogallol, and derivatives of these classes of compound. Inorganic compounds in the form of salts and complexes, such as salts of the metals Mn, Ti, Zr, Hf, V, Co and Ce, also find frequent application. Preference is given in this context to the transition metal salts selected from the group consisting of manganese and/or cobalt salts and/or complexes, with particular preference cobalt ammine complexes, cobalt acetato complexes, cobalt carbonyl complexes, the chlorides of cobalt or of manganese and manganese sulfate. Similarly, zinc compounds may be used to prevent corrosion on the ware.

In terms of their composition, the rinse aid particles of the invention may be designed so that they dissolve to a minor extent, if at all, in the main wash cycle (and also in optional prewash cycles). This ensures that the active substances are not released until the rinse cycle, where they develop their action. In addition to this chemical formulation, a physical formulation may be necessary depending on the type of dishwashing machine, so that the rinse aid particles are not pumped off when the water is changed in the machine and hence are no longer available for the rinse cycle. Standard domestic dishwashing machines, upstream of the detergent-liquor pump, which pumps the water or cleaning solution from the machine after the individual cleaning cycles, comprise a sieve insert, intended to prevent clogging of the pump by food residues. If the user cleans heavily soiled kitchen- and tableware, then this sieve insert requires regular cleaning, which is a simple operation owing to the ease of access and removability. The rinse aid particles of the invention, then, are preferably designed in terms of their size and shape such that they do not pass through the sieve insert of the dishwashing machine even after the cleaning cycle, i.e., after exposure to agitation in

the machine and to the detergent solution. This ensures that rinse aid particles are present in the dishwashing machine in the rinse cycle, these rinse aid particles releasing the active substance(s) under the action of the warmer water and so bringing the desired rinse effect. Particulate machine dishwashing compositions that are preferred in the context of the present invention are those wherein the particulate rinse aid has particle sizes of between 1 and 40 mm, preferably between 1.5 and 30 mm, and in particular between 2 and 20 mm.

In the dishwashing compositions of the invention, the rinse aid particles, having the sizes stated above, may project from the matrix of the other particulate ingredients; alternatively, the other particles may likewise have sizes within the stated range, so that, overall, a detergent is formulated that comprises large detergent particles and rinse aid particles. Especially if the rinse aid particles of the invention are colored, i.e., have red, blue, green, or yellow color, for example, it is advantageous for the appearance of the product, i.e. of the overall detergent, if the rinse aid particles are visibly larger than the matrix comprising the particles of the other ingredients of the detergent. Here, preference is given to inventive particulate machine dishwashing compositions which (without taking into account the rinse aid particles) have particle sizes of between 100 and 3000 μm , preferably between 300 and 2500 μm , and in particular between 400 and 2000 μm .

As well as coloring the rinse aid particles, the visual attractiveness of such compositions may also be enhanced by contrasting coloration of the powder matrix or by the shape of the rinse aid particles. Since it is possible to use technically uncomplicated techniques to produce the rinse aid particles, it is readily possible to offer them in a wide variety of shapes. In addition to the particle

shape which approximates to the spherical form, for example, cylindrical or cuboid particles may be produced and used. Other geometric shapes as well may be realized. Specific product designs may include, for example, star-shaped rinse aid particles. It is also possible without problems to produce disks and shapes with plants and animal bodies as their base, examples being tree, flower, blossom, sheep, fish, etc. Interesting visual attractions may also be created in this way by producing the rinse aid particles in the form of a stylized glass, in order to underscore visually the clear-rinse effect in the product as well. No limits are placed on the imagination in this context.

15 If the detergents of the invention are formulated as a powder mixture, then - especially if there are large differences between the size of rinse aid particles and detergent matrix - on the one hand partial separation may occur when the pack is shaken, and on the other hand dosing may be different in two successive washing operations, since the user does not always automatically dose equal quantities of the detergent and rinse aid particles. If it is desired technically to use an identical quantity for each washing operation, this can be realized by the packaging - familiar to the skilled worker - of the compositions of the invention in water-soluble film bags. The present invention also provides particulate machine dishwashing compositions wherein one dose unit is welded in a water-soluble film bag.

30 By this means, the user need only insert a bag, containing for example a detergent powder and a plurality of visually distinctive rinse aid particles, into the dispenser of his or her dishwashing machine. This embodiment of the present invention is therefore a visually attractive alternative to conventional detergent tablets.

The detergents of the invention may be produced in a manner known per se. A process for producing pulverulent machine dishwashing compositions with clear-rinse effect, in which a conventional pulverulent machine dishwashing composition is mixed with rinse aid particles of the invention, is therefore also provided by the present invention.

10 The desired retention, described earlier on above, of the rinse aid particles in the machine even when the water is changed may be effected not only by the abovementioned enlargement of the rinse aid particles but also by a reduction in the size of the holes in the sieve insert.

15 In this way, it is possible to formulate machine dishwashing compositions having a uniform average particle size of less than, for example, from 4 to 12 mm. For this purpose, a sieve insert which replaces or covers the insert present in the machine is added to the product

20 of the invention wherein the rinse aid particles also have relatively small particle sizes. The present invention therefore additionally provides a kit of parts comprising a pulverulent machine dishwashing composition of the invention and a sieve insert for domestic

25 dishwashing machines.

As already mentioned, the inventive combination of composition and sieve insert makes it possible to formulate compositions in which the rinse aid particles

30 also have relatively small particle sizes. Kits of parts in accordance with the invention wherein the particle sizes of the machine dishwashing composition (including the rinse aid particles) is in the range from 400 to 2500 μm , preferably from 500 to 1600 μm , and in

35 particular from 600 to 1200 μm , are preferred.

In order to prevent clogging of the added sieve insert by residues of soil, the chosen mesh size or hole size should not be too small. Here, preference is given to kits of parts in accordance with the invention wherein
5 the mesh size or hole size of the sieve insert is from 1 to 4 mm and the rinse aid particles are larger than this mesh size or hole size of the sieve insert.

The kit of parts in accordance with the invention is not
10 restricted to the particular form of the sieve insert at which said insert replaces or covers the insert present in the machine. In accordance with the invention it is also possible, and preferred, to enclose with the kit of parts a sieve insert having the form of a basket, which
15 may be suspended in a known manner in the dishwashing machine - on the cutlery basket, for example. In this way, a sieve insert thus designed replaces the dispenser compartment, i.e., the user doses the machine dishwashing composition of the invention directly into this sieve
20 insert, which acts in the manner described above in the washing and rinse cycle.

The advantages associated with the invention may also be utilized when the composition is in the form of the
25 compact tablet. The present invention therefore additionally provides a detergent tablet for machine dishwashing, comprising builders and also, optionally, further detergent ingredients, which comprises diquaternalary polysiloxanes, preferably diquaternalary
30 polysiloxanes of the formula I, with particular preference diquaternalary poly(dimethylsiloxanes) of the formula II, and especially diquaternalary poly(dimethylsiloxanes) of the formula III, in amounts of from 0.5 to 60% by weight, preferably from 1 to 50% by weight, with
35 particular preference from 2.5 to 40% by weight, and in particular from 5 to 30% by weight, based in each case on the tablet weight.

Here again, in respect of preferred embodiments, reference may be made to the above remarks. As already mentioned, the introduction of the diquaternalary polysiloxanes into the rinse cycle is particularly preferred, so that preferred detergent tablets are those comprising the diquaternalary polysiloxanes in dissolution-retarded form.

Particular preference is given in this context not only to a retarded dissolution but also to a controlled release based not on slower solubility but, instead, on a release controlled by external circumstances. The above-described rinse aid particles may also be formulated as a tablet phase and in tablets as well offer the possibility of temperature-controlled release of the diquaternalary polysiloxanes.

The present invention thus further provides multiphase detergent tablets for machine dishwashing, comprising builders and also, optionally, further detergent ingredients, wherein at least one phase comprises

- a) from 0 to 65% by weight of one or more carrier materials,
- b) from 30 to 70% by weight of coating substance(s) having a melting point above 50°C
- c) from 0 to 65% by weight of fatty substance(s),
- d) from 0 to 50% by weight of further active substances and/or auxiliaries, and
- e) from 0.1 to 70% by weight of diquaternalary polysiloxanes.

Entirely in analogy to the above remarks relating to the particulate rinse aid, the same embodiments (amount, nature and formulation of the ingredients, etc.) are also preferred in the case of the tablets of the invention.

In the context of the present invention, the individual phases of the tablet may have different three-dimensional forms. The simplest embodiment is that of two-layer or multilayer tablets, each layer of the tablet constituting one phase. In accordance with the invention, however, it is also possible to prepare multiphase tablets in which individual phases have the form of inclusions into (an) other phase(s). In addition to so-called "ring-core" tablets, possible examples include laminated tablets or combinations of the stated embodiments. Examples of multiphase tablets can be found in the figures of EP-A-0055 100 (Jeyes), which describes toilet cleaning blocks. The most widespread three-dimensional form in the art at present for multiphase tablets is the two-layer or multilayer tablet. In the context of the present invention, therefore, it is preferred for the phases of the tablet to have the form of layers and for the tablet to have 2, 3 or 4 phases.

The tablets of the invention may take on any geometric form whatsoever, with particular preference being given to concave, convex, biconcave, biconvex, cubic, tetragonal, orthorhombic, cylindrical, spherical, cylinder-segmentlike, discoid, tetrahedral, dodecahedral, octahedral, conical, pyramidal, ellipsoid, pentagonal-, heptagonal- and octagonal-prismatic, and rhombohedral forms. It is also possible to realize completely irregular outlines such as arrow or animal forms, trees, clouds, etc. If the tablets of the invention have corners and edges, these are preferably rounded off. As an additional visual differentiation, an embodiment having rounded corners and beveled (chamfered) edges is preferred.

Instead of the layer structure, it is also possible to prepare tablets which comprise the detergent component of the invention in the form of other phases. Here, it has

- 5 been found suitable to prepare base tablets which have one or more cavities, and to insert the melt comprising ingredients a) to d) of the detergent component of the invention into the cavity and allow it to solidify therein. This preparation process produces preferred multiphase detergent tablets comprising a base tablet, which has a cavity, and a part present at least partly in the cavity.
- 10 The cavity in the compressed part of such tablets of the invention may have any form whatsoever. It may go right through the tablet, i.e., have an opening on different sides, for example, at the top and bottom side, of the tablet; alternatively, it may be a cavity which does not
- 15 go through the entire tablet, and whose opening is visible only on one tablet side. The form of the cavity may also be chosen freely within wide limits. For reasons of process economy, continuous holes whose openings are located on opposite faces of the tablets, and depressions
- 20 having an opening at one tablet side, have become established. In preferred detergent tablets, the cavity has the form of a continuous hole whose openings are located on two opposite tablet surfaces. The form of a continuous hole of this kind may be chosen freely,
- 25 preference being given to tablets wherein the continuous hole has circular, ellipsoid, triangular, rectangular, square, pentagonal, hexagonal, heptagonal or octagonal horizontal sections. It is also possible to realize completely irregular hole shapes, such as arrow or animal
- 30 forms, trees, clouds, etc. As with the tablets, preference is given, in the case of angular holes, to those having rounded corners and edges or having rounded corners and chamfered edges.
- 35 The abovementioned geometric embodiments may be combined with one another as desired. For instance, it is just as possible to prepare tablets having a rectangular or

square outline and circular holes as it is to prepare circular tablets having octagonal holes, there being no limits on the diversity of possible combinations. For reasons of process economy and the esthetic perception of the user, hole-type tablets particularly preferred are those wherein the tablet outline and the hole cross section have the same geometric shape, examples being tablets having a square outline and a square hole made centrally therein. Particular preference is given in this context to annular tablets, i.e., circular tablets with a circular hole.

If the aforementioned principle of the hole open at two opposite tablet sides is reduced to an opening, depression tablets are obtained. Detergent tablets of the invention wherein the cavity has the form of a depression are likewise preferred. With this embodiment, as with the "hole tablets", the tablets of the invention may take on any geometric form whatsoever, with particular preference being given to concave, convex, biconcave, biconvex, cubic, tetragonal, orthorhombic, cylindrical, spherical, cylinder-segmentlike, discoid, tetrahedral, dodecahedral, octahedral, conical, pyramidal, ellipsoid, pentagonal-, heptagonal- and octagonal-prismatic, and rhombohedral forms. It is also possible to realize completely irregular outlines such as arrow or animal forms, trees, clouds, etc. If the tablet has corners and edges, these are preferably rounded off. As additional visual differentiation, an embodiment having rounded corners and beveled (chamfered) edges is preferred.

The form of the depression may also be chosen freely, preference being given to tablets in which at least one depression may take on a concave, convex, cubic, tetragonal, orthorhombic, cylindrical, spherical, cylinder-segmentlike, discoid, tetrahedral, dodecahedral, octahedral, conical, pyramidal, ellipsoid, pentagonal-,

heptagonal- and octagonal-prismatic, or rhombohedral form. It is also possible to realize completely irregular depression forms, such as arrow or animal forms, trees, clouds, etc. As with the tablets, depressions having rounded corners and edges or having rounded corners and chamfered edges are preferred.

In the case set out above, the part present at least partially in the cavity consists solely of ingredients a) to d) of the detergent components. It is, however, also possible to introduce support material-based detergent components into the cavity (cavities). For reasons of process economy, however, preference is given to multiphase detergent tablets wherein the part present in the cavity comprises

- a) from 0 to 10% by weight, preferably from 0 to 7.5% by weight, and in particular from 0 to 5% by weight, of one or more carrier materials,
- b) from 30 to 70% by weight, preferably from 35 to 65% by weight, and in particular from 40 to 60% by weight, of coating substance(s) having a melting point above 50°C,
- c) from 0 to 65% by weight, preferably from 10 to 60% by weight, and in particular from 20 to 50% by weight, of fatty substance(s),
- d) from 0 to 50% by weight, preferably from 5 to 45% by weight, and in particular from 10 to 40% by weight, of further additive substances and/or auxiliaries, and
- e) from 0.1 to 70% by weight, preferably from 1 to 50% by weight, and in particular from 5 to 40% by weight, of diquaternary polysiloxanes.

The size of the depression or continuous hole in comparison to the total tablet is guided by the desired end use of the tablets. Depending on with how much further active substance the remaining void volume is to

be filled, and on whether a smaller or larger amount of detergent component is to be present, the size of the cavity may vary. Irrespective of the end use, in preferred detergent tablets the volume ratio of compressed part ("base tablet") to detergent component is from 2:1 to 100:1, preferably from 3:1 to 80:1, with particular preference from 4:1 to 50:1, and in particular from 5:1 to 30:1.

Besides the stated volume ratio, it is also possible to state a mass ratio of the two parts, the two values correlating to one another by way of the densities of the base tablet and, respectively, of the detergent component. Irrespective of the density of the individual parts, preference is given to detergent tablets of the invention wherein the weight ratio of base tablet to detergent component is from 1:1 to 100:1, preferably from 2:1 to 80:1, with particular preference from 3:1 to 50:1, and in particular from 4:1 to 30:1.

Analogous details may also be given for the surfaces visible in each case of the base tablet and, respectively, of the detergent component. Here, preference is given to detergent tablets wherein the outwardly visible surface area of the detergent component accounts for from 1 to 25%, preferably from 2 to 20%, with particular preference from 3 to 15%, and in particular from 4 to 10%, of the total surface area of the tablet.

The detergent component and the base tablet are preferably colored so as to be visually distinguishable. In addition to visual differentiation, performance advantages may be obtained by virtue of different solubilities of the different regions of the tablet. Detergent tablets in which the detergent component dissolves more rapidly than the base tablet are preferred

in accordance with the invention. By incorporating certain constituents, firstly, it is possible to accelerate specifically the solubility of the detergent component; secondly, the release of certain ingredients from the detergent component may lead to advantages in the washing or cleaning process.

Preference is also given, of course, to detergent tablets of the invention wherein the detergent component dissolves later in the wash program than the base tablet. Performance advantages from this retarded release may be achieved, for example, by using a slower-dissolving detergent component to release active substance(s) only in later cycles. Thus in the case of machine dishwashing, for example, it can be ensured by means of slower-dissolving detergent components that further active substance(s) is (are) available in the rinse cycle. By means of additional substances such as nonionic surfactants, acidifiers, soil release polymers, etc., it is possible in this way to enhance the rinse results. The incorporation of perfume is also readily possible; by means of its retarded release it is possible in the case of dishwashing machines to eliminate the "alkali odor" when the machine is opened, which is a frequent occurrence. In relation to the detergent components of the invention, the acidifier, soil release polymer, etc. ingredients are in this case ingredients d).

In preferred embodiments of the present invention the base tablet possesses a high specific weight. The invention prefers detergent tablets wherein the base tablet has a density of more than 1000 g dm^{-3} , preferably more than 1025 g dm^{-3} , with particular preference more than 1050 g dm^{-3} , and in particular more than 1100 g dm^{-3} . In order to facilitate the disintegration of highly compacted tablets, it is possible to incorporate disintegration aids, known as tablet disintegrants, into

the tablets in order to reduce the disintegration times. Tablet disintegrants, or disintegration accelerators, are understood in accordance with Römpp (9th Edition, Vol. 6, p. 4440) and Voigt "*Lehrbuch der pharmazeutischen Technologie*" [Textbook of pharmaceutical technology] (6th Edition, 1987, pp. 182-184) to be auxiliaries which ensure the rapid disintegration of tablets in water or gastric fluid and the release of the drugs in absorbable form.

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These substances increase in volume on ingress of water, with on the one hand an increase in the intrinsic volume (swelling) and on the other hand, by way of the release of gases, the generation of a pressure which causes the tablets to disintegrate into smaller particles. Examples of established disintegration aids are carbonate/citric acid systems, with the use of other organic acids also being possible. Examples of swelling disintegration aids are synthetic polymers such as polyvinylpyrrolidone (PVP) or natural polymers and/or modified natural substances such as cellulose and starch and their derivatives, alginates, or casein derivatives.

15

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Preferred detergent tablets contain from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight, of one or more disintegration aids, based in each case on the tablet weight. If only the base tablet comprises disintegration aids, then these figures are based only on the weight of the base tablet. If disintegration aids are incorporated into the detergent components of the invention, they count as ingredient d).

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Preferred disintegrants used in the context of the present invention are cellulose-based disintegrants and so preferred detergent tablets comprise a cellulose-based disintegrant of this kind in amounts from 0.5 to 10% by

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weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight. Pure cellulose has the formal empirical composition $(C_6H_{10}O_5)_n$ and, considered formally, is a β -1,4-polyacetal of cellobiose, which
5 itself is constructed of two molecules of glucose. Suitable celluloses consist of from about 500 to 5000 glucose units and, accordingly, have average molecular masses of from 50,000 to 500,000. Cellulose-based disintegrants which can be used also include, in the
10 context of the present invention, cellulose derivatives obtainable by polymer-analogous reactions from cellulose. Such chemically modified celluloses include, for example, products of esterifications and etherifications in which hydroxyl hydrogen atoms have been substituted. However,
15 celluloses in which the hydroxyl groups have been replaced by functional groups not attached by an oxygen atom may also be used as cellulose derivatives. The group of the cellulose derivatives embraces, for example, alkali metal celluloses, carboxymethyl cellulose (CMC),
20 cellulose esters and cellulose ethers, and aminocelluloses. Said cellulose derivatives are preferably not used alone as cellulose-based disintegrants but instead are used in a mixture with cellulose. The cellulose derivative content of these
25 mixtures is preferably less than 50% by weight, with particular preference less than 20% by weight, based on the cellulose-based disintegrant. The particularly preferred cellulose-based disintegrant used is pure cellulose, free from cellulose derivatives.

30 The cellulose used as disintegration aid is preferably not used in finely divided form but instead is converted into a coarser form, for example, by granulation or compaction, before being admixed to the premixes intended
35 for compression. Detergent tablets comprising disintegrants in granular or optionally cocranulated form are described in German Patent Applications

DE 197 09 991 (Stefan Herzog) and DE 197 10 254 (Henkel) and in International Patent Application WO98/40463 (Henkel). These documents also provide further details on the production of granulated, compacted or cogranulated cellulose disintegrants. The particle sizes of such disintegrants are usually above 200 μm , preferably between 300 and 1600 μm to the extent of at least 90% by weight, and in particular between 400 and 1200 μm to the extent of at least 90% by weight. The abovementioned, relatively coarse cellulose-based disintegration aids, and those described in more detail in the cited documents, are preferred for use as disintegration aids in the context of the present invention and are available commercially, for example, under the designation Arbocel[®] TF-30-HG from the company Rettenmaier.

As a further cellulose-based disintegrant or as a constituent of this component it is possible to use microcrystalline cellulose. This microcrystalline cellulose is obtained by partial hydrolysis of celluloses under conditions which attack only the amorphous regions (approximately 30% of the total cellulose mass) of the celluloses and break them up completely but leave the crystalline regions (approximately 70%) intact. Subsequent deaggregation of the microfine celluloses resulting from the hydrolysis yields the microcrystalline celluloses, which have primary particle sizes of approximately 5 μm and can be compacted, for example, to granules having an average particle size of 200 μm .

Detergent tablets which are preferred in the context of the present invention further comprise a disintegration aid, preferably a cellulose-based disintegration aid, preferably in granular, cogranulated or compacted form, in amounts of from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight, based in each case on the tablet weight.

The detergent tablets of the invention may further comprise, both in the base tablet and in the detergent component, a gas-evolving effervescent system. Said gas-evolving effervescent system may consist of a single substance which on contact with water releases a gas. Among these compounds mention may be made, in particular, of magnesium peroxide, which on contact with water releases oxygen. Normally, however, the gas-releasing effervescent system consists in its turn of at least two constituents which react with one another and, in so doing, form gas. Although a multitude of systems which release, for example, nitrogen, oxygen or hydrogen are conceivable and practicable here, the effervescent system used in the detergent tablets of the invention will be selectable on the basis of both economic and environmental considerations. Preferred effervescent systems consist of alkali metal carbonate and/or alkali metal hydrogen carbonate and of an acidifier apt to release carbon dioxide from the alkali metal salts in aqueous solution.

Among the alkali metal carbonates and/or alkali metal hydrogen carbonates, the sodium and potassium salts are much preferred over the other salts on grounds of cost. It is of course not mandatory to use the pure alkali metal carbonates or alkali metal hydrogen carbonates in question; rather, mixtures of different carbonates and hydrogen carbonates may be preferred from the standpoint of wash technology.

In preferred detergent tablets, the effervescent system used comprises from 2 to 20% by weight, preferably from 3 to 15% by weight, and in particular from 5 to 10% by weight, of an alkali metal carbonate or alkali metal hydrogen carbonate, and from 1 to 15, preferably from 2

to 12, and in particular from 3 to 10% by weight of an acidifier, based in each case on the total tablet.

5 As examples of acidifiers which release carbon dioxide from the alkali metal salts in aqueous solution it is possible to use boric acid and also alkali metal hydrogen sulfates, alkali metal dihydrogen phosphates, and other inorganic salts. Preference is given, however, to the use of organic acidifiers, with citric acid being a particularly preferred acidifier. However, it is also possible, in particular, to use the other solid mono-, 10 oligo- and polycarboxylic acids. Preferred among this group, in turn, are tartaric acid, succinic acid, malonic acid, adipic acid, maleic acid, fumaric acid, oxalic acid, and polyacrylic acid. Organic sulfonic acids such as amidosulfonic acid may likewise be used. A commercially available acidifier which is likewise preferred for use in the context of the present invention is Sokalan® DCS (trademark of BASF), a mixture of 15 succinic acid (max. 31% by weight), glutaric acid (max. 50% by weight), and adipic acid (max. 33% by weight).

In the context of the present invention, preference is given to detergent tablets where the acidifier used in the effervescent system comprises a substance from the 25 group of the organic di-, tri- and oligocarboxylic acids, or mixtures thereof.

Following production, the particulate detergents and/or 30 detergent tablets of the invention, and the novel detergent components per se, may be packed, the use of certain packaging systems having proven particularly useful. The present invention additionally provides a combination comprising (a) particulate detergent(s) and/or (a) detergent tablet(s) of the invention and a 35 packaging system containing said detergent and/or said detergent tablet(s), said packaging system having a

moisture vapor transmission rate of from 0.1 g/m²/day to less than 20 g/m²/day if said packaging system is stored at 23°C and a relative equilibrium humidity of 85%.

5 The packaging system of the combination of detergent component and/or detergent and/or detergent tablet(s) and packaging system has, in accordance with the invention, a moisture vapor transmission rate of from 0.1 g/m²/day to less than 20 g/m²/day when said packaging system is
10 stored at 23°C and a relative equilibrium humidity of 85%. These temperature and humidity conditions are the test conditions specified in **DIN Standard 53122**, which allows minimal deviations (23 ± 1°C, 85 ± 2% relative humidity). The moisture vapor transmission rate of a
15 given packaging system or material may be determined in accordance with further standard methods and is also described, for example, in **ASTM Standard E-96-53T** ("Test for measuring water vapor transmission of materials in sheet form") and in **TAPPI Standard T464 m-45** ("Water
20 vapor permeability of sheet materials at high temperature and humidity"). The measurement principle of common techniques is based on the water uptake of anhydrous calcium chloride which is stored in a container in the appropriate atmosphere, the container being closed at the
25 top face with the material to be tested. From the surface area of the container closed with the material to be tested (permeation area), the weight gain of the calcium chloride, and the exposure time, the moisture vapor transmission rate may be calculated as follows:

30

$$MVPR = \frac{24 \cdot 10000}{A} \cdot \frac{x}{y} [g/m^2/24h]$$

35 where A is the area of the material to be tested in cm², x is the weight gain of the calcium chloride in g, and y is the exposure time in h.

The relative equilibrium humidity, often referred to as "relative atmospheric humidity", is 85% at 23°C when the moisture vapor transmission rate is measured in the context of the present invention. The ability of air to accommodate water vapor increases with temperature up to a particular maximum content, the so-called saturation content, and is specified in g/m³. For example, 1 m³ of air at 17° is saturated with 14.4 g of water vapor; at a temperature of 11°, saturation is reached with just 10 g of water vapor. The relative atmospheric humidity is the ratio, expressed as a percentage, of the actual water vapor content to the saturation content at the prevailing temperature. If, for example, air at 17° contains 12 g/m³ water vapor, then the relative atmospheric humidity (RH) = $(12/14.4) \cdot 100 = 83\%$. If this air is cooled, then saturation (100% RH) is reached at what is known as the dew point (in the example: 14°), i.e., on further cooling a precipitate is formed in the form of mist (dew). The humidity is determined quantitatively using hygrometers and psychrometers.

The relative equilibrium humidity of 85% at 23°C can be established precisely, for example, in laboratory chambers with humidity control, to +/-2% RH depending on the type of apparatus. In addition, constant and well-defined relative atmospheric humidities are formed in closed systems at a given temperature over saturated solutions of certain salts, these humidities deriving from the phase equilibrium between water partial pressure, saturated solution, and sediment.

The combinations of the invention may of course in turn be packaged in secondary packaging, examples being cardboard packaging or trays, there being no need to impose further requirements on the secondary packaging. The secondary packaging, accordingly, is possible but not necessary.

Packaging systems which are preferred in the context of the present invention have a moisture vapor transmission rate of from 0.5 g/m²/day to less than 15 g/m²/day.

5
Depending on the embodiment of the invention, the packaging system of the combination of the invention contains a defined amount of novel detergent component, a defined amount of a particulate detergent composition, or
10 one or more detergent tablets. In accordance with the invention it is preferred either to design a tablet such that it comprises one application unit of the detergent, and to package this tablet individually, or to pack into one packaging unit the number of tablets which totals one
15 application unit. In the case of an intended dose of 80 g of detergent, therefore, it is possible in accordance with the invention to produce and package individually one detergent tablet weighing 80 g, but in accordance with the invention it is also possible to package two
20 detergent tablets each weighing 40 g into one pack in order to arrive at a combination in accordance with the invention. This principle can of course be extended, so that, in accordance with the invention, combinations may also comprise three, four, five or even more detergent
25 tablets in one packaging unit. Of course, two or more tablets in a pack may have different compositions. In this way it is possible to separate certain components spatially from one another in order, for example, to avoid stability problems.

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The packaging system of the combination of the invention may consist of a very wide variety of materials and may adopt any desired external forms. For reasons of economy and of greater ease of processing, however, preference is
35 given to packaging systems in which the packaging material has a low weight, is easy to process, and is inexpensive. In combinations which are preferred in

accordance with the invention, the packaging system consists of a bag or pouch of single-layer or laminated paper and/or polymer film.

5 The detergent tablets may be filled unsorted, i.e. as a loose heap, into a pouch made of said materials. On
10 esthetic grounds and for the purpose of sorting the combinations into secondary packaging, however, it is preferred to fill the detergent tablets individually, or
15 sorted into groups of two or more, into bags or pouches. For individual application units of the detergent tablets which are located in a bag or pouch, a term which has become established in the art is that of the "flow pack". Flow packs of this kind may optionally then - again,
20 preferably sorted - be packaged into outer packaging, which underscores the compact commercial form of the tablet.

20 The single-layer or laminated paper or polymer film bags or pouches preferred for use as packaging systems may be designed in a very wide variety of ways: for example, as inflated pouches without a center seam or as pouches with a center seam which are sealed by means of heat (heat, sealing), adhesives, or adhesive tapes. Single-layer
25 pouch and bag materials include the known papers, which may if appropriate be impregnated, and also polymer films, which may if appropriate be coextruded. Polymer films that can be used as a packaging system in the context of the present invention are specified, for
30 example, in *Hans Domininghaus, "Die Kunststoffe und ihre Eigenschaften", 3rd edition, VDI Verlag, Düsseldorf, 1988, page 193.* Figure 111 shown therein also gives indications of the water vapor permeability of the materials mentioned.

35 Combinations which are particularly preferred in the context of the present invention comprise as packaging

system a bag or pouch of single-layer or laminated polymer film having a thickness of from 10 to 200 μm , preferably from 20 to 100 μm , and in particular from 25 to 50 μm .

5

Although it is possible in addition to the abovementioned films and papers also to use wax-coated papers in the form of cardboard packaging as a packaging system for the detergent tablets, it is preferred in the context of the present invention for the packaging system not to comprise any cardboard boxes made of wax-coated paper. In the context of the present invention, the term "packaging system" always relates to the primary packaging of the detergent component, composition or tablets, i.e., to the packaging whose inner face is in direct contact with the detergent component, composition or tablet surface. No requirements whatsoever are imposed on any optional secondary packaging, so that all customary materials and systems can be used in this case.

20

As already mentioned earlier on above, the detergent components, detergent compositions, or detergent tablets of the combination in accordance with the invention comprise further ingredients of detergents, in varying amounts, depending on their intended use. Independently of the intended use of the compositions or tablets, it is preferred in accordance with the invention for the detergent composition(s) or tablet(s) to have a relative equilibrium humidity of less than 30% at 35°C.

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The relative equilibrium humidity of the detergent compositions or tablets may be determined in accordance with common methods, the following procedure having been chosen in the context of the present investigations: a water-impermeable 1 liter vessel with a lid which has a closable opening for the introduction of samples was filled with a total of 300 g of detergent tablets and

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held at a constant 23°C for 24 h in order to ensure a uniform temperature of vessel and substance. The water vapor pressure in the space above the tablets can then be determined using a hygrometer (Hygrotest 6100, Testoterm Ltd, England). The water vapor pressure is then measured every 10 minutes until two successive values show no deviation (equilibrium humidity). The abovementioned hygrometer permits direct display of the recorded values in % relative humidity.

Likewise preferred are embodiments of the combination in accordance with the invention wherein the packaging system is of resealable configuration. Combinations wherein the packaging system has a microperforation may also be realized with preference in accordance with the invention.

As mentioned earlier on above, detergent components, detergent compositions or detergent tablets for machine dishwashing may be prepared by the processes of the invention. Accordingly, the present invention additionally provides a method of cleaning kitchen- and tableware in a dishwashing machine, which comprises placing one or more particulate detergents and/or one or more detergent tablets of the invention in the dispensing compartment of the dishwashing machine and running a wash program in the course of which the dispensing compartment opens and the detergent(s) and/or tablet(s) is or are dissolved.

With the cleaning method of the invention as well it is possible to forego the dispensing compartment and to place the detergent components and/or detergent compositions or the tablet(s) of the invention, for example, in the cutlery basket. Here again, of course, the use of a dosing aid, for example, a basket insert which is placed in the washing compartment, is possible

without problems. Accordingly, the present invention further provides a method of cleaning kitchen- and tableware in a dishwashing machine, which comprises placing one or more particulate detergents of the invention and/or one or more detergent tablets of the invention, with or without a dosing aid, in the washing compartment of the dishwashing machine and running a wash program in the course of which the detergent(s) and/or the tablet(s) is or are dissolved.

Examples:

Ware stained with standard stains (see below) was washed using a standard commercial machine dishwashing composition in powder form (dosage: 25 g), and in the Comparative Example, V, a standard commercial rinse aid was metered in from the reservoir tank of the machine. In the inventive Example, E, the standard commercial rinse aid of the comparative example was upgraded prior to use by adding Tegopren® 6922 (diquateryary poly(dimethylsiloxane) of the formula III with stearyl radicals R, acetate ions X⁻ and a value for n of 30, from Th. Goldschmidt AG). In both cases, the dosage of the rinse aid was 5 ml per rinse cycle; in the inventive example, E, 1 gram of Tegopren® 6922 was introduced into the rinse cycle by the rinse aid dosing. The machine used was a Miele G 590 with a universal program; the water hardness was 16°d [German hardness].

The ware washed in this way was stained again with standard stains and washed again under the conditions described above. After that, the cleaning performance of the washes was evaluated on the basis of the evaluation scale described below. The results of this evaluation are indicated in the following table.

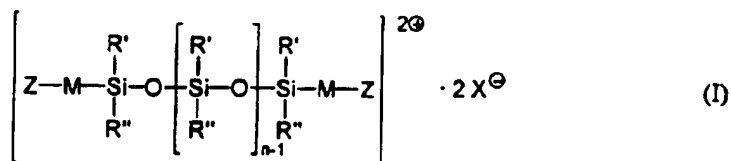
	V	E
Minced meat on glass (baked on)	8.8	10.0
Minced meat on porcelain (dried on)	8.5	10.0
Oat flakes	7.2	9.2
Milk (baked on)	7.4	9.3

5 The standard stains were applied by a standardized
 procedure which is described in "Methoden zur Bestimmung
 der Reinigungsleistung von maschinellen
 Geschirrspülmitteln" [Methods of determining the cleaning
 performance of machine dishwashing compositions] (Part A:
 SÖFW-Journal, vol. 124 11/98, pages 706 to 713; Part B:
 SÖFW-Journal, vol. 124 14/98, pages 1022 to 1034). Also
 10 disclosed therein are the evaluation criteria in
 accordance with which the evaluations listed in the above
 table were made.

15 The table clearly shows that the ware treated in
 accordance with the invention can be cleaned much better
 in subsequent washes than the ware of the comparative
 example.

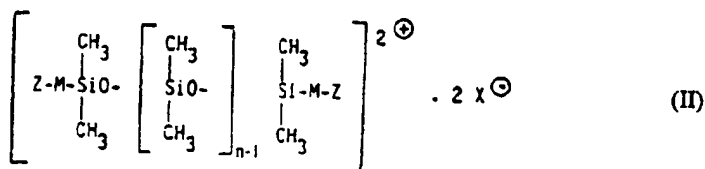
Claims:

1. The use of diquaternary polysiloxanes in machine dishwashing compositions.
2. The use of diquaternary polysiloxanes in the rinse cycle during machine dishwashing.
3. The use as claimed in either of claims 1 or 2 of one or more diquaternary polysiloxanes of the formula I,

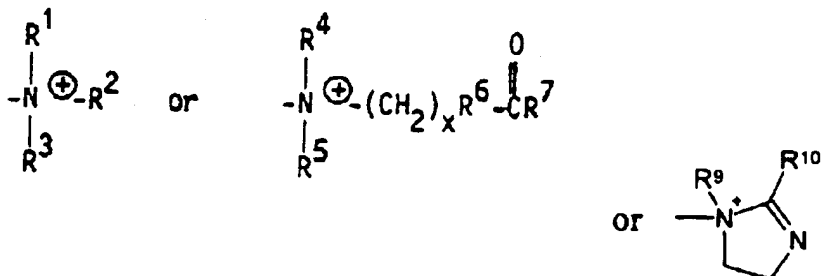


in which Z is a quaternized nitrogen center,
 R' and R'' independently of one another are
 a C₁₋₄ alkyl radical or an aryl
 radical,
 M is a divalent hydrocarbon radical
 with at least 4 carbon atoms, which
 preferably has at least one hydroxyl
 group and may be interrupted by one
 or more oxygen atoms and/or groups of
 the type -C(O)-, -C(O)O- or -C(O)N-,
 n is a number from 1 to 201, and
 X⁻ is an organic or inorganic anion.

4. The use as claimed in any of claims 1 to 3 of one or more diquaternary poly(dimethylsiloxanes) of the formula II,



in which Z is the radical



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R^1 , R^2 , R^3 , R^4 , R^5 , R^7 , R^9 and R^{10} independently of one another are C_{1-22} alkyl or C_{2-22} alkylene radicals without or with one or more hydroxyl groups or radicals $-\text{CH}_2\text{-aryl}$,

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R^6 is an oxygen atom or a group $-\text{N}(\text{R}^8)$, R^8 being a C_{1-4} alkyl or hydroxyalkyl radical or hydrogen,

M is a divalent hydrocarbon radical with at least 4 carbon atoms, and may be interrupted by one or more oxygen atoms and/or groups of the type $-\text{C}(\text{O})-$, $-\text{C}(\text{O})\text{O}-$ or $-\text{C}(\text{O})\text{N}-$,

15

n is a number from 1 to 201 and

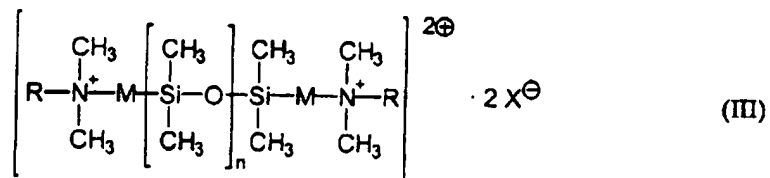
X^- is an organic or inorganic anion.

5. The use as claimed in claim 4, wherein R^1 , R^2 and R^3 have at least 10 carbon atoms or one of R^1 , R^2 and R^3 is a benzyl radical; and M has at least one hydroxyl group.

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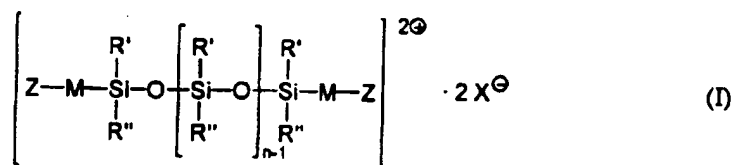
6. The use as claimed in any of claims 1 to 5 of one or more diquatary poly(dimethylsiloxanes) of the formula III,

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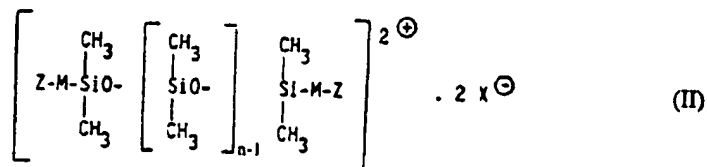
in which R is a C₆₋₂₂ alkyl or alkylene radical,
M is a spacer of the formula
CH₂CH(OH)CH₂O(CH₂)₃,
n is a number from 1 to 100, and
X⁻ is an organic or inorganic anion.

7. The use as claimed in claim 5, wherein R is a stearyl radical, n is a number selected from 10, 30 or 50 and X⁻ is an acetate ion.
8. A rinse aid composition for machine dishwashing, comprising diquatertiary polysiloxanes.
9. The rinse aid composition as claimed in claim 8, comprising one or more diquatertiary polysiloxanes of the formula I,



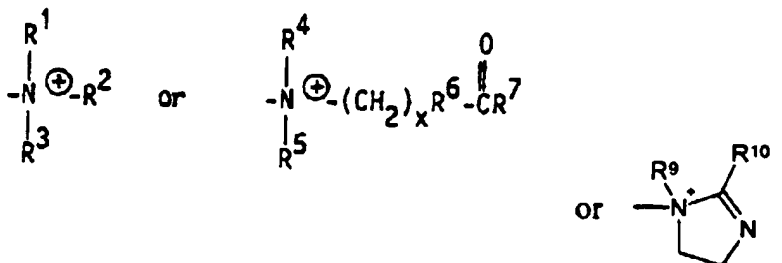
in which Z is a quaternized nitrogen center,
R' and R'' independently of one another are a C₁₋₄ alkyl radical or an aryl radical,
M is a divalent hydrocarbon radical with at least 4 carbon atoms, and may be interrupted by one or more oxygen atoms and/or groups of the type -C(O)-, -C(O)O- or -C(O)N-,
n is a number from 1 to 201, and
X⁻ is an organic or inorganic anion,

preference being given to rinse aid compositions comprising one or more diquateryary poly(dimethylsiloxanes) of the formula II,



5

in which Z is the radical



10

$\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^7, \text{R}^9$ and R^{10} independently of one another are C_{1-22} alkyl or C_{2-22} alkylene radicals without or with one or more hydroxyl groups or radicals $-\text{CH}_2\text{-aryl}$,

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R^6 is an oxygen atom or a group $-\text{N}(\text{R}^8)$, R^8 being a C_{1-4} alkyl or hydroxyalkyl radical or hydrogen,

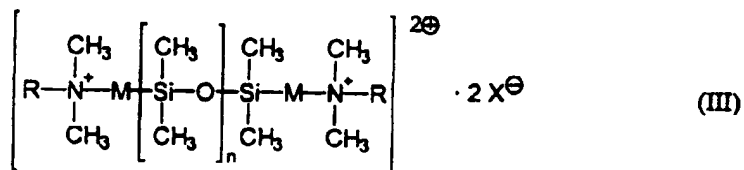
M is a divalent hydrocarbon radical with at least 4 carbon atoms, and may be interrupted by one or more oxygen atoms and/or groups of the type $-\text{C}(\text{O})-$, $-\text{C}(\text{O})\text{O}-$ or $-\text{C}(\text{O})\text{N}-$,

20

n is a number from 1 to 201 and

X^- is an organic or inorganic anion,

and compositions comprising one or more diquateryary poly(dimethylsiloxanes) of the formula III,



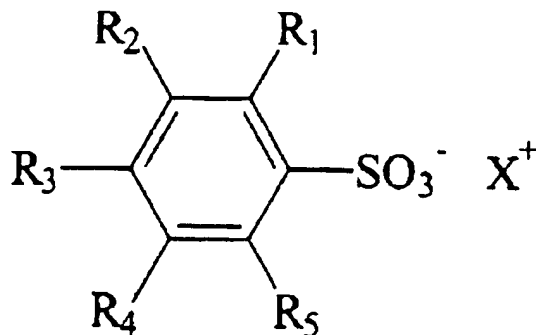
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in which R is a C₆₋₂₂ alkyl or alkylene radical,
M is a spacer of the formula
 $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_3$,
n is a number from 1 to 100, and
5 X⁻ is an organic or inorganic anion.

10. The rinse aid composition as claimed in claim 9,
wherein in formula III, R is a stearyl radical, n is
10, 30 or 50, and X⁻ is an acetate ion.
- 10 11. The rinse aid composition as claimed in any of
claims 8 to 10, comprising the diquatertiary poly-
siloxane(s) in amounts of from 0.001 to 20% by
weight, based on the rinse aid composition.
- 15 12. The rinse aid composition as claimed in claim 11,
wherein the amounts are from 0.01 to 10% by weight.
13. The rinse aid composition as claimed in claim 11,
wherein the amounts are from 0.1 to 5% by weight.
- 20 14. The rinse aid composition as claimed in claim 11,
wherein the amounts are from 0.15 to 2.5% by weight.
- 25 15. The rinse aid composition as claimed in any of
claims 8 to 14, comprising surfactant(s), in amounts
of from 0.1 to 40% by weight, based on the rinse aid
composition.
- 30 16. The rinse aid composition as claimed in claim 15,
wherein nonionic surfactants are present.
17. The rinse aid composition as claimed in claim 16,
wherein the nonionic surfactants are selected from
alkoxylated alcohols.

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18. The rinse aid composition as claimed in claims 15 to 17, wherein the amounts are from 0.5 to 30% by weight.
- 5 19. The rinse aid composition as claimed in claims 15 to 17, wherein the amounts are from 1 to 20% by weight.
20. The rinse aid composition as claimed in claims 15 to 17, wherein the amounts are from 2 to 15% by weight.
- 10 21. The rinse aid composition as claimed in any of claims 8 to 20, comprising nonaqueous solvent(s), preferably ethanol, n-propanol, i-propanol, 1-butanol, 2-butanol, glycol, propanediol, 15 butanediol, glycerol, diglycol, propyl diglycol, butyl diglycol, hexylene glycol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ether, dipropylene glycol methyl or ethyl ether, methoxy-, ethoxy- or butoxytriglycol, 20 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol t-butyl ether, and 25 mixtures of these solvents.
22. The rinse aid composition as claimed in any of claims 8 to 21, comprising solubilizers selected from aromatic sulfonates of the formula
- 30



in which each of the radicals R_1 , R_2 , R_3 , R_4 and R_5 independently of one another is selected from H or a C_{1-5} alkyl or alkenyl radical and X is a cation.

- 5
23. The rinse aid composition as claimed in any of claims 8 to 22, comprising acidifiers selected from organic acids.
- 10 24. The rinse aid composition as claimed in claim 23, wherein the organic acids are selected from adipic acid, amidosulfonic acid, succinic acid, citric acid, fumaric acid, maleic acid, malonic acid, oxalic acid, and tartaric acid, and also mixtures of
- 15 these acids.
25. The rinse aid composition as claimed in any of claims 8 to 24, further comprising one or more substances from the groups of the soil release polymers, the dyes, and the fragrances.
- 20
26. A particulate rinse aid for machine dishwashing, comprising
- 25 a) from 0 to 65% by weight of one or more carrier materials,
- b) from 30 to 70% by weight of coating substance(s) having a melting point of more than 50°C ,
- c) from 0 to 65% by weight of fatty substance(s),
- 30 d) from 0 to 50% by weight of further active substances and/or auxiliaries, and

e) from 0.1 to 70% by weight of diquaternary polysiloxane.

- 5 27. The particulate rinse aid as claimed in claim 26, comprising diquaternary polysiloxanes, in amounts of from 0.5 to 60% by weight, based on the particulate rinse aid.
- 10 28. The particulate rinse aid as claimed in claim 27, wherein the diquaternary polysiloxanes are selected from diquaternary polysiloxanes of the formula I as defined in claim 8.
- 15 29. The particulate rinse aid as claimed in claim 27, wherein the diquaternary poly(dimethyl-siloxanes) are selected from diquaternary poly(dimethyl-siloxanes) of the formula II as defined in claim 8.
- 20 30. The particulate rinse aid as claimed in claim 27, wherein the diquaternary poly(dimethylsiloxanes) are selected from diquaternary poly(dimethylsiloxanes) of the formula III as defined in claim 8 or 9.
- 25 31. The particulate rinse aid as claimed in any of claims 27 to 30, wherein the amounts are from 1 to 50% by weight.
- 30 32. The particulate rinse aid as claimed in any of claims 27 to 30, wherein the amounts are from 2.5 to 40% by weight.
- 35 33. The particulate rinse aid as claimed in any of claims 27 to 30, wherein the amounts are from 5 to 30% by weight.
34. The particulate rinse aid as claimed in any of claims 26 to 33, comprising as ingredient b) one or

more substances having a melting range of between 50 and 100°C as coating substances.

- 5 35. The particulate rinse aid as claimed in claim 34, wherein the melting range is between 52.5 and 80°C.
36. The particulate rinse aid as claimed in claim 34, wherein the melting range is between 55 and 75°C.
- 10 37. The particulate rinse aid as claimed in any of claims 34 to 36, wherein the coating substances are paraffin waxes having a melting range of from 50°C to 65°C and/or substances from the group of the polyethylene glycols (PEGs) and/or polypropylene glycols (PPGs).
- 15 38. The particulate rinse aid as claimed in any of claims 26 to 37, further comprising as ingredient d) surfactant(s), in amounts of from 5 to 47.5% by weight, based on the particulate rinse aid.
- 20 39. The particulate rinse aid as claimed in claim 38, wherein nonionic surfactant(s) are present.
- 25 40. The particulate rinse aid as claimed in claim 39, wherein the nonionic surfactant(s) are alkoxylated alcohols.
- 30 41. The particulate rinse aid as claimed in any of claims 30 to 40, wherein the amounts are from 10 to 45% by weight.
- 35 42. The particulate rinse aid as claimed in any of claims 30 to 40, wherein the amounts are from 15 to 42.5% by weight.

43. The particulate rinse aid as claimed in any of claims 30 to 40, wherein the amounts are from 20 to 40% by weight.
- 5 44. A detergent tablet for machine dishwashing, comprising builders and also, optionally, further detergent ingredients, which comprises diquaternary polysiloxanes, selected from diquaternary polysiloxanes of the formula I, diquaternary poly(dimethyl-siloxanes) of the formula II, and
10 diquaternary poly(dimethylsiloxanes) of the formula III, as defined in claim 8, in amounts of from 0.5 to 60% by weight, based on the tablet weight.
- 15 45. A detergent tablet as claimed in claim 44, wherein the amounts are from 1 to 50% by weight.
46. A detergent tablet as claimed in claim 44, wherein the amounts are from 2.5 to 40% by weight.
- 20 47. A detergent tablet as claimed in claim 44, wherein the amounts are from 5 to 30% by weight.
48. The detergent tablet as claimed in any of claims 44 to 47, comprising the diquaternary polysiloxanes in
25 dissolution-retarded form.
49. A multiphase detergent tablet for machine dishwashing, comprising builders and also,
30 optionally further detergent ingredients, wherein at least one phase comprises
a) from 0 to 65% by weight of one or more carrier materials,
b) from 30 to 70% by weight of coating substance(s)
35 having a melting point above 50°C
c) from 0 to 65% by weight of fatty substance(s),

- d) from 0 to 50% by weight of further active substances and/or auxiliaries, and
- e) from 0.1 to 70% by weight of diquaternalary polysiloxanes.

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50. The multiphase detergent tablet as claimed in claim 49, wherein the phases have the form of layers and the tablet has 2, 3 or 4 phases.

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51. The multiphase detergent tablet as claimed in claim 49, comprising a base tablet, which has a cavity, and a part present at least partly in the cavity.

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52. The multiphase detergent tablet as claimed in claim 51, wherein the part present in the cavity comprises

a) from 0 to 10% by weight, of one or more carrier materials,

b) from 30 to 70% by weight, of coating substance(s) having a melting point above 50°C,

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c) from 0 to 65% by weight, of fatty substance(s),

d) from 0 to 50% by weight, of further additive substances and/or auxiliaries, and

e) from 0.1 to 70% by weight, of diquaternalary polysiloxanes.

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53. A tablet as claimed in claim 51, wherein the part present in the cavity comprises

a) from 0 to 7.5% by weight, of one or more carrier materials,

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b) from 35 to 65% by weight, of coating substance(s) having a melting point above 50°C,

c) from 10 to 60% by weight, of fatty substance(s),

d) from 0 to 50% by weight, of further additive substances and/or auxiliaries, and

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e) from 1 to 50% by weight, of diquaternalary polysiloxanes.

54. A tablet as claimed in claim 51, wherein the part present in the cavity comprises
- a) from 0 to 5% by weight, of one or more carrier materials,
 - 5 b) from 40 to 60% by weight, of coating substance(s) having a melting point above 50°C,
 - c) from 20 to 50% by weight, of fatty substance(s),
 - d) from 10 to 40% by weight, of further additive substances and/or auxiliaries, and
 - 10 e) from 5 to 40% by weight, of diquatarnary polysiloxanes.

